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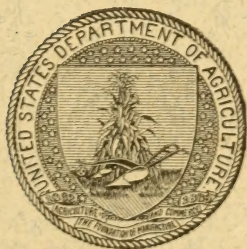
U. S. DEPARTMENT OF AGRICULTURE,  
BUREAU OF CHEMISTRY—BULLETIN No. 113.  
H. W. WILEY, Chief of Bureau.

INJURY TO VEGETATION AND ANIMAL LIFE  
BY SMELTER WASTES.

By

J. K. HAYWOOD,

CHIEF OF THE MISCELLANEOUS LABORATORY.

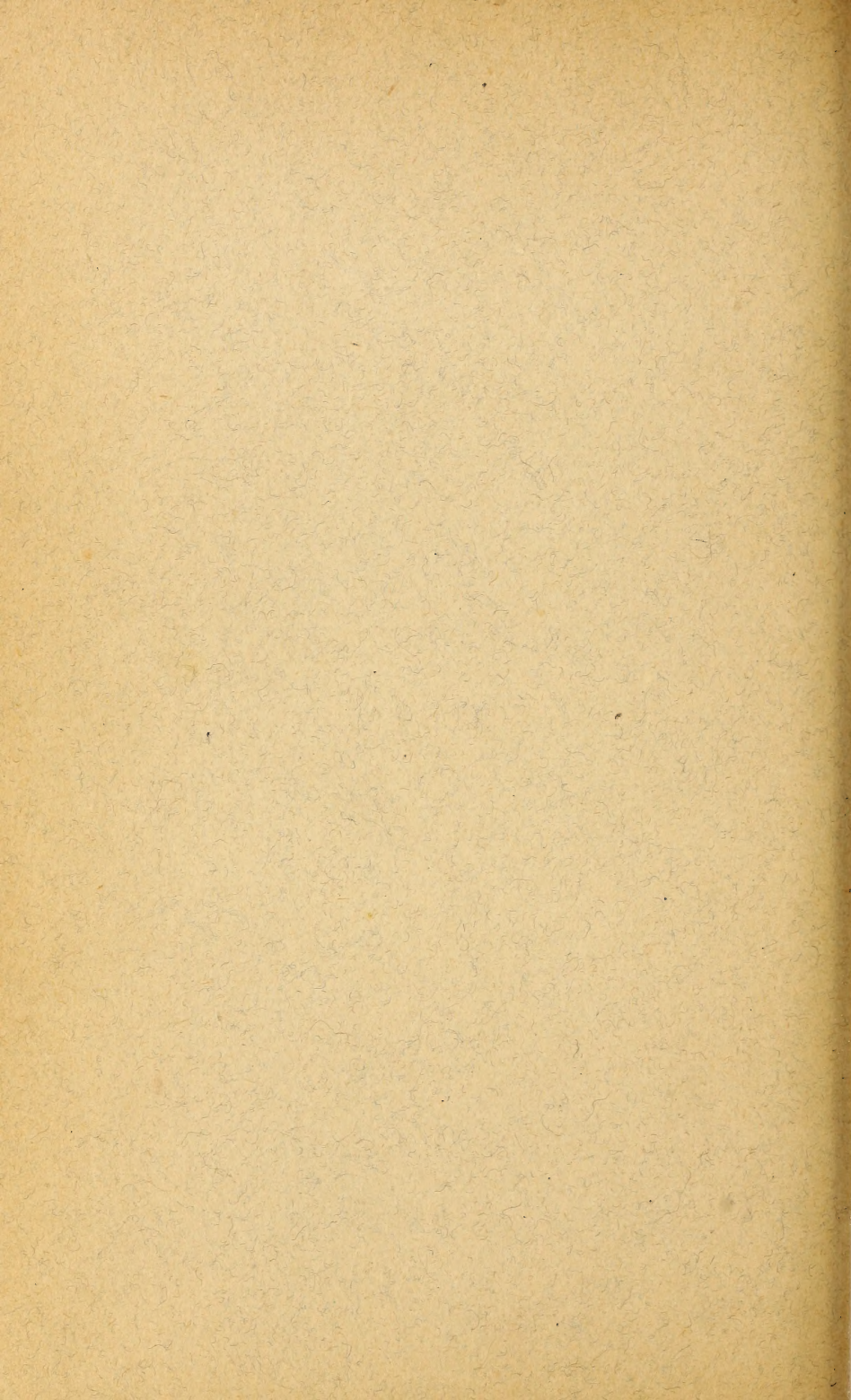


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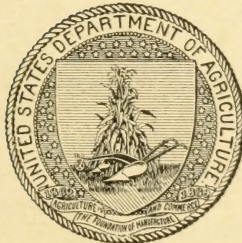
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## LETTER OF TRANSMITTAL.

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UNITED STATES DEPARTMENT OF AGRICULTURE,  
BUREAU OF CHEMISTRY,  
*Washington, D. C., April 11, 1908.*

SIR: I have the honor to submit for your approval the results of certain investigations made by the Chief of the Miscellaneous Laboratory of this Bureau in regard to the injury to vegetation and animal life observed in the vicinity of certain smelters, particularly one located at Anaconda, Mont. This report covers one of a series of such investigations dealing with the injury caused by smelter wastes, which have been conducted in this Bureau from time to time during the past six years, with a view to cooperating with the Bureau of Forestry in the preservation of the forests and protecting the farming interests. I recommend that this report be published as Bulletin 113 of the Bureau of Chemistry.

Respectfully,

H. W. WILEY,  
*Chief of Bureau.*

HON. JAMES WILSON,  
*Secretary of Agriculture.*

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# INJURY TO VEGETATION AND ANIMAL LIFE BY SMELTER WASTES.

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## INTRODUCTION.

### PROCESS OF EXTRACTING METALS FROM ORES.

Before considering the injurious effects which wastes from plants smelting sulphid copper ores may have on vegetation and animal life, a brief account will be given of the process generally used to extract the metal from the ores. For this purpose an outline of the process followed at Anaconda, Mont., will be given, which, though differing in some details from the process used at other plants, is based on the same general principles and produces similar waste products.

The ores when they arrive at the plant are graded as first and second class, the former being sent to the bins of the blast furnaces and the latter to the concentrator bins. The second-class ores are next sampled, crushed, and passed over jigs, by which process a product richer in copper, known as the "concentrates," is obtained.

The reject from the jigs is crushed again and passed over jigs fitted with finer screens, "concentrates" being again obtained. After extracting all that can be taken out by the jigs, the ore is again crushed and passed over the Wilfley tables, thus giving rise to the "table concentrates." The concentrates are sent to a bin at the foot of the concentrator. There remain in the water used for concentration some fine particles of valuable material, and this is allowed to flow into ponds outside the plant, where the fine particles settle out in the form of "slimes" and the water is finally drawn off. The slimes are briquetted and blast-smelted. The waste products from the concentration are known as "tailings." These tailings, consisting principally of silica, iron, etc., with small quantities of copper and arsenic, in case the latter is present, are discharged on the dump heap.

The concentrates are dumped into roasting furnaces, where large quantities of sulphur and arsenic are driven off, the former as sulphur dioxide and trioxide and the latter in volatile form. The residue, now known as "calcine," is transferred to reverberatory furnaces. This process yields (1) a slag consisting principally of silicates of iron and calcium with very small quantities of copper; (2) a product richer in copper known as "matte;" and (3) volatile

arsenic and sulphur products which are carried to the flue. The slag is granulated in water and passed to the dump. The "matte" is carried to the converters, where it is treated in the same way as "matte" from the blast furnaces.

The blast furnace receives a charge consisting essentially of the high-grade ores, converter slag, briquettes of siliceous fines and slimes from the concentrator, limestone, and coke. A large part of the sulphur passes off to the flue as sulphur dioxid and trioxid, and large amounts of arsenic are volatilized. The iron and silica in the ore, together with the lime, form a slag (containing a very small amount of copper) which is granulated in water and carried to the dump; the copper forms a "matte" consisting principally of a combination of copper, iron, and sulphur. This, together with the "matte" from the reverberatory furnaces, is next carried to the converters, the lining of which is a siliceous material that lasts for several runs.

In the converter the sulphur which is present in the "matte" is oxidized to sulphur dioxid and trioxid and escapes up the flue, the remaining arsenic is volatilized and also goes up the flue, while the iron unites with the siliceous lining to form a slag which is returned to the blast furnaces, since it is a good flux and also contains considerable quantities of copper. The copper obtained by this process is carried to the preliminary refining apparatus, where air is passed over the molten mass to remove traces of sulphur and the small amount of slag which was not taken out in the converters is also eliminated. During this process some copper oxid is formed, but upon stirring this is again reduced to copper by the carbon of the converter poles. In this condition the copper is cast into ingots, which are sold to refineries not situated at Anaconda.

The fumes from these processes are passed through long cooling chambers in order to condense the volatilized compounds of arsenic as far as possible, but in spite of this precaution large amounts of arsenic escape from the top of the chimney. No attempt is made to recover any of the sulphur compounds.

#### RESULTANT WASTES.

From this brief description of the process used at Anaconda, it will be evident that four wastes arise which may be injurious to plant or animal life.

(1) The sulphur contained in the ore is gradually given off during the various processes of smelting, as sulphur dioxid and a little sulphur trioxid, which would have their injurious action on vegetation.



(2) In case arsenic is present in the ores, as it often is and notably at Anaconda, it is given off in the fumes from the smelter in volatile form and deposited on the surrounding land and crops, where it may be present in sufficient amounts to poison cattle browsing on exposed ranges, or living on hay cut from such pasture.

(3) The tailings from the water concentration of the ore and the slag, in a finely divided condition, are discharged on a dump heap through which the water from the plant is constantly percolating on its course to adjacent streams and the "slimes" are left in piles in the open air. Both the slime heap and the dump are also exposed to the percolating action of the rain. In consequence, the streams receiving the waste water from concentrating and smelting plants contain a comparatively large amount of copper in suspension and are apt to hold some copper in solution. If these streams are used for irrigating purposes there is a possible source of injury to growing crops due to the action of the copper present.

(4) Finely divided particles of the ore are discharged from the smelter stack and settle on the surrounding country. These fine particles of flue dust may contain sufficient amounts of copper, lead, and zinc to injure vegetation, because of their toxic action through the medium of the soil and because of their caustic action on the foliage. While it is believed by some<sup>a</sup> that the action of this so-called flue dust gives rise to the principal damage caused by smelter smoke, the writer is inclined to the opinion<sup>b</sup> that such injury is not of great significance except in a very limited area about the smelter, and that an investigation of it is in most cases unnecessary, as the owners of smelters are usually perfectly willing to admit damage, even beyond the area likely to be affected by the solid particles of copper, lead, and zinc in the flue dust.

In the first case of this kind studied by the writer in the vicinity of Redding, Cal. (see Pl. I), and in the laboratory at Washington during 1903 and 1904, no complaint had been made of the injury from arsenic or from copper, so that the only problem considered was the action of sulphur dioxide and trioxide fumes on the surrounding vegetation. The results of this study and the original investigations connected therewith have been published,<sup>c</sup> but a résumé will be given, together with certain results obtained since the publication of the Redding investigations, in order that the reader may understand the present status of the work.

<sup>a</sup> Ebaugh, J. Amer. Chem. Soc., 1907, 29: 951.

<sup>b</sup> Haywood, Science, 1907, 26: 476.

<sup>c</sup> U. S. Dept. Agr., Bureau of Chemistry, Bul. 89, Injury to Vegetation by Smelter Fumes, 1905.



## EXPERIMENTAL INVESTIGATIONS RELATING TO THE ACTION OF SULPHUR DIOXID ON VEGETATION.

### ORGANS OF THE PLANT THROUGH WHICH INJURY TAKES PLACE.

In carrying on an investigation of this kind it was first necessary to ascertain whether or not sulphur dioxid was injurious to plant life, how small a quantity was injurious, and through what organs of the plant such injury took place. Light is thrown on this subject by the work of foreign chemists.

Freytag<sup>a</sup> showed that sulphur dioxid and trioxid do not injure the plant through the roots. His experiment consisted in watering wheat, oats, and peas with large amounts of dilute sulphurous acid in one case and sulphuric acid in another. The plants neither wilted nor reduced their yield. Von Schroeder and Schmitz-Dumont<sup>b</sup> made an investigation on pines, firs, lindens, and Norway maples in 1896, in which they treated (1) the aerial parts of the plants with sulphur dioxid, (2) the aerial parts of the plant and the earth with sulphur dioxid, and (3) the earth in which the plant was growing with dilute sulphurous acid. They also showed that the injury to vegetation by sulphur dioxid is not through the roots, but through the medium of the leaves, and that even extremely minute quantities of sulphur dioxid are injurious.

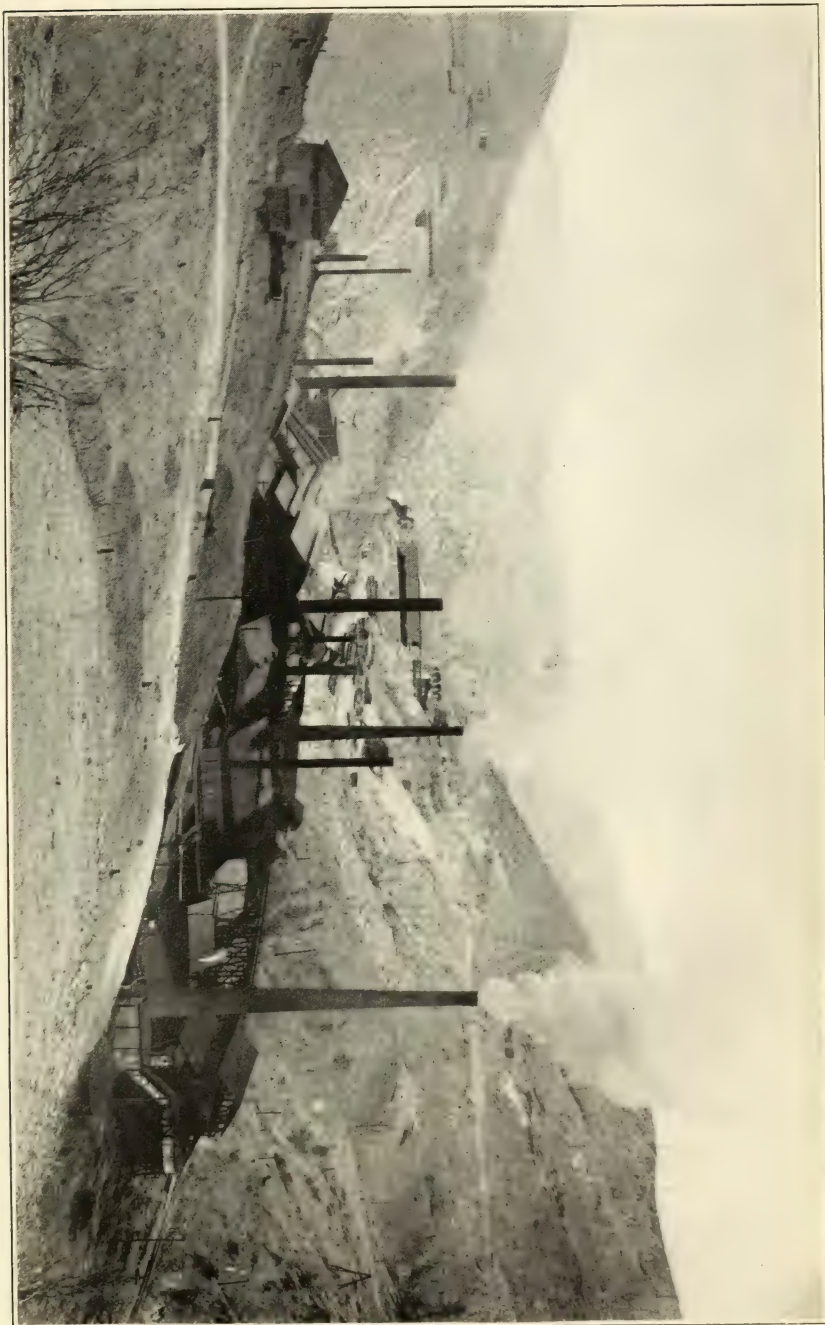
Wieler in his work entitled "Untersuchungen über die Einwirkung schwefliger Säure auf die Pflanzen," which has been published since the work at Redding was done, also gives numerous experiments to show that minute amounts of sulphur dioxid injure plants through the leaves, but he also states that in the course of time the sulphur dioxid and trioxid present in smelter smoke injuriously affect the soil and so indirectly injure the plant through the roots. He is further of the opinion that soils subjected to the action of sulphur dioxid suffer from a reduction in the lower forms of animal and plant life which are so necessary to the series of natural changes taking place in normal soils. He is also of the opinion that such soils suffer a loss in bases, which eventually causes them to become acid, as not enough bases are present to form humates with the humic acid. In proof of the latter point, he has taken soil samples from the vicinity of several smelters and found that all of them contained free humic acid.

Wieler's conception of this additional injurious action of sulphur dioxid on the soil has been published so recently that the writer has not been able to investigate the subject sufficiently to express a defi-

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<sup>a</sup> Mitt. d. königl. landw. Akad., Poppelsdorf, 1869.

<sup>b</sup> Thar. forstl. Jahrb., 1896, 46: 1.



KESWICK SMELTER, NEAR REDDING, CAL., IN OPERATION.





nite opinion in regard to its merits. It would appear, however, from the work done that Wieler lays too much stress on the sulphur dioxide injury to the soil, as compared with the injury caused by the sulphur dioxide acting on the foliage. In support of this opinion several soils from the vicinity of a smelter were tested by the author. These soils were taken from forest land where certain trees were practically annihilated by smelter fumes, as proved by chemical analysis, and yet all of the soils gave an alkaline reaction, showing that there had evidently not been such a loss of bases as to give rise to free humic acid.

On the whole, then, the work done undoubtedly points to the fact that sulphur dioxide injures vegetation through the leaves, but whether it injures the soil, and so indirectly injures the plant through the roots, is a problem which must be studied further before a definite conclusion can be reached.

#### AMOUNT OF SULPHUR DIOXID THAT MAY CAUSE INJURY.

In regard to the amounts of sulphur dioxide in the atmosphere that may injure vegetation, Stöckhardt<sup>a</sup> showed that 1 part of sulphur dioxide to 1,000,000 parts of air injured potted pines seriously after 365 fumigations. Freyag<sup>a</sup> cast doubt on Stöckhardt's data by his investigations, and Stöckhardt's work was repeated by Von Schroeder and Schmitz-Dumont,<sup>a</sup> who showed that great injury was inflicted by fumigating pines 109 times with 1 part of sulphur dioxide to 100,000 parts of air and that injury was to be noted on fumigating pines 583 times with 1 part of sulphur dioxide to 1,000,000 parts of air.

The details of the work done by the writer in relation to injury to pines and young cowpeas<sup>b</sup> by sulphur dioxide show the following results:

(1) Pine trees fumigated<sup>c</sup> 6 times with 1 part of sulphur dioxide to 100 parts of air showed marked injury. All of the needles were drooping, and nearly all had turned yellow or brown.

(2) Pine trees fumigated 9 times with 1 part of sulphur dioxide to 1,000 parts of air were greatly injured in the same manner as the plants just described.

(3) Pine trees fumigated 50 times with 1 part of sulphur dioxide to 10,000 parts of air were badly injured.

(4) Cowpeas fumigated 18 times with 1 part of sulphur dioxide to 10,000 parts of air lost all their leaves and could not be revived, although carefully watered and tended outside the fumigation chamber.

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<sup>a</sup> Haselhoff and Lindau, Die Beschädigung der Vegetation durch Rauch, pp. 58-66.

<sup>b</sup> U. S. Dept. Agr., Bureau of Chemistry, Bul. 89.

<sup>c</sup> Each fumigation lasted for one hour.

(5) Pine trees fumigated 50 times with 1 part of sulphur dioxid to 30,000 parts of air showed decided injury.

Since the above work was performed in connection with the investigation of 1903-4, described in Bulletin 89, the writer has conducted further experiments (during 1907) to test the effect of sulphur dioxid on vegetation. A fumigation chamber was used consisting of a wooden frame 3 feet broad, 3 feet deep, and 4 feet in height, with glass panes, as shown in Plate II. On the side was a removable door which could be tightly closed. This chamber was placed over various trees about 3 feet in height, just as they grew in the open. The sulphur dioxid was prepared by burning carbon bisulphid, in an alcoholic solution, in such amounts as would give definite amounts of sulphur dioxid in relation to the space within the chamber. A fan, run by dry batteries from the outside, was used to mix the sulphur dioxid and the air. Each fumigation was continued for one hour, when the chamber was removed and the plant allowed to stand in the open from fifteen minutes to an hour. The chamber was entirely removed from the plants at night.

Another fumigation chamber of exactly the same construction and size was placed over a control plant. In this chamber the same amount of alcohol was burned as was used in the case of those plants which were subjected to the action of sulphur dioxid. A fan was also used to mix the products of combustion of the alcohol with the air present, and the periods of fumigation were the same in both cases. In this way the control plants were subjected to the same conditions as the treated plants except for the presence of a definite quantity of sulphur dioxid.

Following are the results obtained on fumigating several different trees which were growing in their natural state in the open:

*No. 5282. Black oak.*—Fumigated 4 times July 8 and 9 with sulphur dioxid 1:1,000. After 1 fumigation the leaves were wilted and streaked. After 4 fumigations the leaves were dry and brown. The control plant was uninjured.

*No. 5284. White oak.*—Fumigated 5 times July 10 and 11 with sulphur dioxid 1:1,000. After 3 fumigations the leaves looked gray and withered. After 5 fumigations the leaves were gray and dry. The control plant was uninjured.

*No. 5286. Cedar.*—Fumigated twice on July 13 with sulphur dioxid 1:1,000. After 2 fumigations the leaves looked brown and drooped. On standing over July 14 the leaves appeared brown and dry. The control plant was uninjured.

*No. 5288. Chestnut.*—Fumigated 5 times on July 15 with sulphur dioxid 1:1,000. After 2 fumigations the leaves began to turn yellow. After 5 fumigations the leaves were yellow and dry. The control plant was uninjured.

*No. 5290. Black oak.*—Fumigated 14 times from July 16 to July 19 with sulphur dioxid 1:10,000. After 11 fumigations the leaves were turning brown and new leaves and sprouts had died. After 14 fumigations all leaves were brown and dry. The control plant was uninjured.



FUMIGATION CHAMBER FOR TESTING EFFECTS OF SULPHUR DIOXID ON YOUNG TREES.





No. 5292. *White oak*.—Fumigated 16 times from July 20 to July 24 with sulphur dioxid 1:10,000. After 2 fumigations brown spots appeared on the leaves. After 5 fumigations the top leaves were dry and brown. After 16 fumigations all the leaves were dry and brown. The control plant was uninjured.

No. 5294. *Scrub pine*.—Fumigated twice on July 25 with sulphur dioxid 1:10,000. After 2 fumigations all the leaves were brown, dry, and dead. The control plant was uninjured.

No. 5296. *Black oak*.—Fumigated 100 times from August 5 to August 30 with sulphur dioxid, 1:50,000. After 29 fumigations the gloss disappeared from the leaves and the young leaves took on a grayish tint. After 100 fumigations all the end buds were killed. The younger leaves were bleached and dotted with brown spots. The old leaves had lost their gloss and were bleached in spots. This tree was observed for three weeks after its removal from the fumigation chamber and no new growth took place. The control plant was uninjured.

No. 5298. *Scrub pine*.—Fumigated 34 times from September 3 to September 10 with sulphur dioxid 1:50,000. After 9 fumigations the top needles were somewhat bleached. After 19 fumigations the top needles were entirely killed and the lower needles were killed at the ends. After 34 fumigations all leaves were brown and dry. The control plant was uninjured.

No. 5300. *Scrub pine*.—Fumigated 96 times from September 12 to October 7 with sulphur dioxid 1:100,000. After 49 fumigations the ends of the young needles were turning brown. After 96 fumigations all the leaves were badly affected, the young needles were brown and dead, the older needles dead at the ends. The control plant was uninjured.

The investigation of the effect of fumigation on plants growing in the open was discontinued at this point on account of a pressure of other work, but will probably be resumed later and even greater dilutions than 1:100,000 will be used.

#### SULPHUR-TRIOXID CONTENT OF THE FOLIAGE OF FUMIGATED AND UNFUMIGATED PLANTS.

It was next necessary to determine whether treating plants with sulphur dioxid increased the sulphur-trioxid content of the leaves so that it was present in larger quantities in the leaves of the treated plants than in those of the untreated ones. As a necessary consequence of such an increase, the sulphur-trioxid content of the ash of the fumigated plants would be apt to be higher than that of the ash of the unfumigated plants.

In the work of Von Schroeder and Schmitz-Dumont, previously mentioned, when different parts of the plants were treated with varying strengths of sulphur dioxid, the sulphur-trioxid content of the treated plants was in excess of that of the control plants in every case, and the percentage of sulphur trioxid in the ash of the treated plants was higher than that in the ash of the control plants. The same was found to be true on making analyses of the pines and cow-peas fumigated by the writer.<sup>a</sup> Analyses of fumigated plants grown

<sup>a</sup> Haywood, U. S. Dept. Agr., Bureau of Chemistry, Bul. 89, p. 14.

in the open, made during 1907 since Bulletin 89 was published, give the following results:

TABLE 1.—*Effect of fumigating trees growing in the open with varying strengths of sulphur dioxide, as shown by the sulphur trioxide determined in the foliage.*

[Calculated to dry basis.]

Serial No.	Description.	Ash in dry leaves.	Sulphur trioxide—	
			In leaves.	In ash.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
5282	Black oak treated with sulphur dioxide 1:1,000.....	3.89	0.70	17.99
5283	Black oak used as control.....	3.68	.59	16.03
5284	White oak treated with sulphur dioxide 1:1,000.....	6.49	2.01	30.97
5285	White oak used as control.....	5.94	.57	9.59
5286	Cedar treated with sulphur dioxide 1:1,000.....	5.46	.48	8.79
5287	Cedar used as control.....	6.06	.35	5.77
5288	Chestnut treated with sulphur dioxide 1:1,000.....	4.49	1.44	32.07
5289	Chestnut used as control.....	4.60	.56	12.17
5290	Black oak treated with sulphur dioxide 1:10,000.....	4.00	.73	18.25
5291	Black oak used as control.....	5.55	.56	10.09
5292	White oak treated with sulphur dioxide 1:10,000.....	5.02	.69	13.74
5293	White oak used as control.....	6.41	.56	8.73
5294	Scrub pine treated with sulphur dioxide 1:10,000.....	2.39	.48	20.08
5295	Scrub pine used as control.....	2.25	.42	18.66
5296	Black oak treated with sulphur dioxide 1:50,000.....	3.64	.56	15.38
5297	Black oak used as control.....	3.98	.50	12.57
5298	Scrub pine treated with sulphur dioxide 1:50,000.....	2.51	.47	18.72
5299	Scrub pine used as control.....	2.69	.35	13.01
5300	Scrub pine treated with sulphur dioxide 1:100,000.....	1.96	.43	21.94
5301	Scrub pine used as control.....	2.05	.31	15.12

It will at once be seen from the foregoing table that all of the plants growing in the open which were treated with sulphur dioxide contained more sulphur trioxide in their leaves than the control plants, and that the percentage of sulphur trioxide in the ash of fumigated plants is higher than it is in those not fumigated. These results at once suggest a method for determining whether trees around a smelter were killed by the fumes or died from other causes.

## FIELD INVESTIGATIONS OF THE ACTION OF SULPHUR DIOXIDE FUMES ON VEGETATION.

### A CALIFORNIA SMELTER AND CERTAIN FOREIGN SMELTERS.

The next step in the investigation was to determine whether the dead and badly injured trees around the smelting works near Redding, Cal., usually contained more sulphur trioxide than trees of the same species which stood close by in the same soil, but were not killed. Of 25 pairs of trees examined in various directions from the smelter 80 per cent contained more sulphur trioxide in the leaves of the injured trees than in the leaves of the uninjured ones, while 20 per cent showed the reverse. It was further shown that in 80 per cent of the cases the injured trees contained a larger percentage of sulphur trioxide in the ash of the leaves than did the uninjured trees.<sup>a</sup>

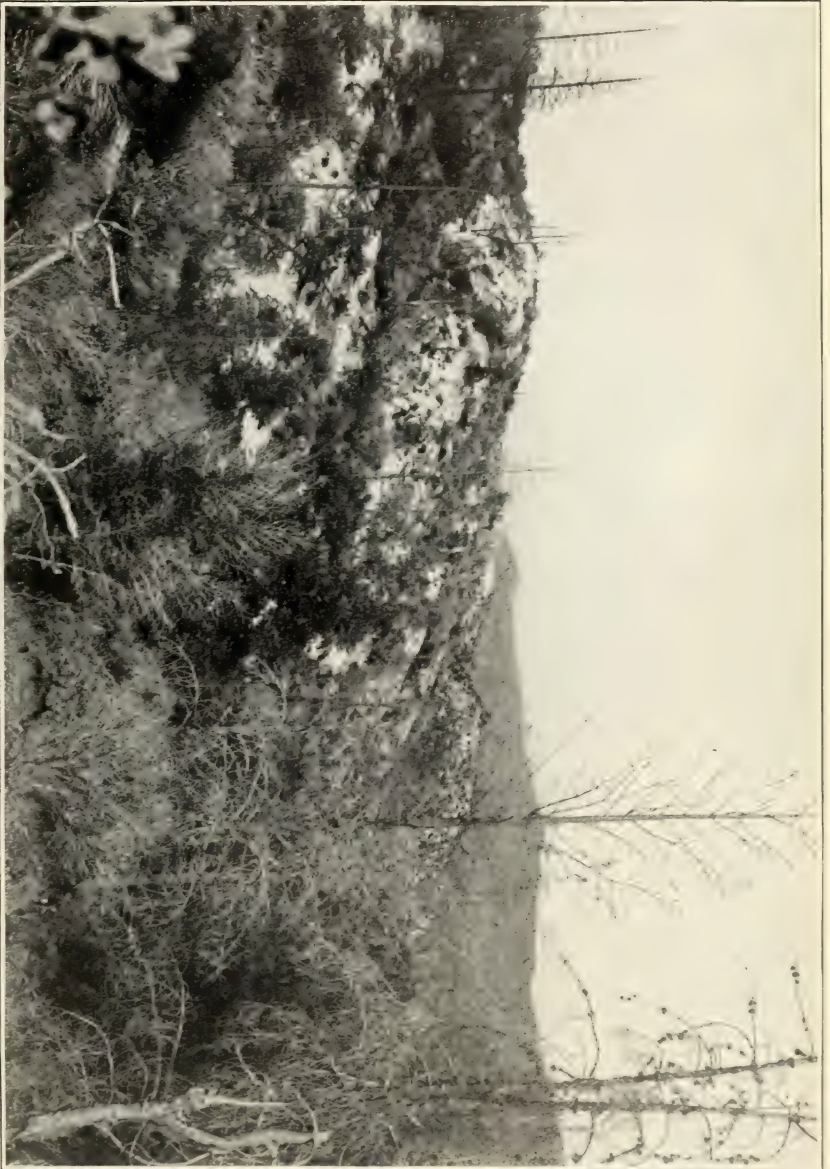
<sup>a</sup> U. S. Dept. Agr., Bureau of Chemistry, Bul. 89.





VIEW ABOUT 2 MILES SOUTH OF KESWICK SMELTER, NEAR REDDING, CAL.





VIEW ABOUT 3 MILES WEST OF KESWICK SMELTER, NEAR REDDING, CAL.





In a similar investigation in the vicinity of a zinc smelter at Lethmathe, Germany,<sup>a</sup> one especially conclusive examination was made of the foliage of the surrounding vegetation. The investigator, instead of selecting the trees in groups of two from the same location, one injured and the other uninjured, used injured trees from points near the smelter and uninjured trees for comparison at points farther distant from the smelter, but in the same direction. (When this can be done the results are even more conclusive than those obtained by the writer by the method just outlined, but, unfortunately, the rugged nature of the country in the vicinity of the smelter at Redding made such a procedure impracticable.) Of nine groups of trees examined 89 per cent contained more sulphur trioxid both in the leaves themselves and in the ash of the leaves of the injured trees than in the uninjured ones. Three or four years later the same region around the zinc smelter was again examined, and it was found that in nineteen groups of trees the leaves of all of the injured trees contained more sulphur trioxid than those of the uninjured ones.

From the work done in the vicinity of Redding, Cal., the following important conclusions are drawn:

(1) Sulphur dioxid when present in very minute amounts in the air kills vegetation.

(2) The injury is accompanied by an increased sulphur trioxid content of the foliage.

(3) The vegetation around the smelter for at least  $3\frac{1}{2}$  miles north, 9 miles south,  $2\frac{1}{2}$  miles east, and 5 to 6 miles west, is greatly injured, and less severe injury extends even beyond these limits for a considerable distance (Pls. III and IV).

#### TWO TENNESSEE SMELTERS.

The next investigation of injury to vegetation by smelter fumes, conducted by the writer, was made in 1905 and the summer of 1906 in the mountainous country of Tennessee, North Carolina, and Georgia, surrounding two Tennessee smelters, and in the laboratory at Washington. The following counties were examined in the various trips made in the vicinity of the smelters: Polk, Tenn.; Fannin and Gilmer, Ga., and Cherokee, N. C. Again, the only injury studied was that due to the action of sulphur dioxid and trioxid on vegetation. The chemist in this investigation was accompanied by one of the foresters of the Department of Agriculture. Samples of soil and foliage were collected for chemical examination, but the foliage came only from those trees which the forester was reasonably sure had not died from insect pests, forest fires, crowding, or other conditions

<sup>a</sup> Haselhoff and Lindau, Die Beschädigung der Vegetation durch Rauch.

commonly causing the destruction of forests. These samples of foliage were classified by the forester and forwarded to the Bureau of Chemistry for analysis.

For purposes of investigation samples of the dead and injured trees surrounding the smelters were examined, as well as of the uninjured trees of the same species beyond the range of apparent injury. The sulphur trioxid content of the foliage and ash of the two sets of samples was then compared. The soils beneath the injured trees were compared with those from beneath the uninjured trees to determine whether any increase in the sulphur trioxid content of the injured trees might be due to an increased amount of sulphur trioxid in the soil.

If the sulphur trioxid content of the uninjured trees, situated much farther away from the smelters, is less than that of the injured trees situated near the smelters, and yet the sulphur trioxid content of the soils in which the trees grow is the same, or nearly the same, in both cases, this increase of sulphur trioxid must have been absorbed from the air and must be responsible, wholly or partly, for the death of the trees, since it is known that small amounts of sulphur dioxid and trioxid, when absorbed by the leaves of trees, do kill them. In the absence of insect pests in sufficient numbers to cause great injury, of forest fires, or other ordinary causes for the death of trees, it must be concluded that it was the sulphur dioxid and trioxid alone that caused the damage.

Attention is again called to the fact that this method of comparing injured trees with uninjured trees at a greater distance from the smelter is better than the method followed by the writer at Redding, Cal.,<sup>a</sup> and should undoubtedly be followed in all cases where such a comparison is possible. The country around the Tennessee smelters easily lent itself to carrying out the investigation in this way, while in the country around Redding, Cal., such a method of working out the problem would have been extremely difficult.

In Table II are given the results obtained by examining the foliage of the injured and uninjured trees for sulphur trioxid and ash. In a northerly, easterly, and westerly direction the writer collected and examined samples from beyond the range of apparent significant injury. In a southerly direction a few such samples were collected, but unfortunately they were very wet when gathered and molded during transit. However, since the samples collected beyond the apparent range of injury in an easterly direction grew in a soil containing practically the same amounts of sulphur trioxid as the soils south of the smelters, and also since the examined area to the south is near the area over which the samples were collected east of the smelters, it

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<sup>a</sup> U. S. Dept. Agr., Bureau of Chemistry, Bul. 89.



is believed that the injured trees to the south can be compared with the uninjured trees beyond the range of significant damage in an easterly direction with perfect satisfaction, and that the results of such a comparison will be just as accurate as though such uninjured samples had been taken beyond the smoke range to the south.

It should be borne in mind that two smelters were involved in the above investigation, which were situated so close to one another that it was impossible to say which probably was causing the damage. Hence a point midway between the two was chosen as the most convenient point from which to reckon all of the distances given in Table II.

TABLE II.—Sulphur trioxid in foliage, in ash, and in soils around smelters.

[Calculated to dry basis.]

## NORTH OF SMELTERS.

Field No.	Serial No.	Description of sample.	Approximate distance and direction from smelters.	Ash in leaves and needles.	Sulphur trioxid—		
					In leaves.	In ash.	In soil.
				<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
51	2797	Foliage, black oak, injured.	7 miles NNW	4.13	0.91	22.03	
60	2806	do.	do	4.62	1.05	22.72	
61	2807	do.	do	4.98	1.10	22.08	
79	2825	Foliage, black oak, uninjured.	13½ miles NNE	4.04	.41	10.14	
59	2805	Soil beneath Nos. 51, 60, 61					0.05
80	2826	Soil beneath No. 79					.03
63	2809	Foliage, scrub pine, injured.	6½ miles NNE	2.83	.87	30.74	
64	2810	do.	do	2.34	.69	29.48	
65	2811	do.	do	2.99	.93	31.10	
78	2824	Foliage, scrub pine, uninjured.	13½ miles NNE	2.06	.36	17.47	
67	2813	Soil beneath Nos. 63, 64, 65					.07
80	2826	Soil beneath No. 78					.03
68	2814	Foliage, white pine, injured.	8 miles NNE	2.46	.66	26.82	
77	2823	Foliage, white pine, uninjured.	13½ miles NNE	1.74	.36	20.69	
71	2817	Soil beneath No. 68					.06
80	2826	Soil beneath No. 77					.03
69	2815	Foliage, black oak, injured.	8 miles NNE	5.20	.95	18.26	
79	2825	Foliage, black oak, uninjured.	13½ miles NNE	4.04	.41	10.14	
71	2817	Soil beneath No. 69					.06
80	2826	Soil beneath No. 78					.03
100	2846	Foliage, white pine, injured.	8½ miles NNE	1.97	.56	28.42	
77	2823	Foliage, white pine, uninjured.	13½ miles NNE	1.74	.36	20.69	
98	2844	Foliage, black oak, injured.	9½ miles NNE	4.41	.75	17.00	
79	2825	Foliage, black oak, uninjured.	13½ miles NNE	4.04	.41	10.14	
81	2827	Foliage, black oak, injured.	12½ miles N. by E.	4.55	.59	12.96	
83	2829	do.	do	4.96	.67	13.50	
79	2825	Foliage, black oak, uninjured.	13½ miles NNE	4.04	.41	10.14	
89	2835	Soil beneath Nos. 81, 83					.03
80	2826	Soil beneath No. 79					.03
90	2836	Foliage, scrub pine, injured.	12½ miles N. by E.	3.07	.51	16.61	
78	2824	Foliage, scrub pine, uninjured.	13½ miles NNE	2.06	.36	17.47	
89	2835	Soil beneath No. 90					.03
80	2826	Soil beneath No. 78					.03
92	2838	Foliage, white pine, injured.	12½ miles N. by E.	2.57	.49	13.06	
93	2839	do.	do	2.39	.50	20.92	
94	2840	do.	do	2.65	.50	18.86	
77	2823	Foliage, white pine, uninjured.	13½ miles NNE	1.74	.36	20.69	

TABLE II.—Sulphur trioxid in foliage, in ash, and in soils around smelters—  
Continued.

## EAST OF SMELTERS.

Field No.	Serial No.	Description of sample.	Approximate distance and direction from smelters.	Ash in leaves and needles.	Sulphur trioxid—		
					In leaves.	In ash.	In soil.
149	2895	Foliage, white oak, injured.	3 miles ENE	<i>Per cent.</i> 3.74	<i>Per cent.</i> 0.85	<i>Per cent.</i> 22.72	-----
158	2904	Foliage, white oak, uninjured.	8½ miles E	4.78	.58	12.13	-----
153	2899	Foliage, shortleaf pine, injured.	4½ miles E	3.53	.61	17.28	-----
154	2900	do	do	3.28	.70	21.34	-----
153	2899	Foliage, shortleaf pine, uninjured.	8½ miles E	2.82	.40	14.18	-----
156	2902	Soil beneath Nos. 153, 154.	-----	-----	-----	-----	0.04
161	2907	Soil beneath No. 157	-----	-----	-----	-----	.04
171	2917	Foliage, shortleaf pine, injured.	5½ miles NE	4.16	.80	19.23	-----
157	2903	Foliage, shortleaf pine, uninjured.	8½ miles E	2.82	.40	14.18	-----
175	2921	Soil beneath No. 171	-----	-----	-----	-----	.06
161	2907	Soil beneath No. 157	-----	-----	-----	-----	.04
164	2910	Foliage, shortleaf pine, injured.	5 miles E	3.53	.83	23.51	-----
157	2903	Foliage, shortleaf pine, uninjured.	8½ miles E	2.82	.40	14.18	-----
166	2912	Foliage, black oak, injured.	5 miles E	5.14	.71	13.81	-----
159	2905	Foliage, black oak, uninjured.	8½ miles E	3.15	.49	15.55	-----
168	2914	Soil beneath Nos. 164, 166.	-----	-----	-----	-----	.06
161	2907	Soil beneath Nos. 157, 159	-----	-----	-----	-----	.04
176	2922	Foliage, black oak, injured.	6 miles NE	5.34	.94	17.60	-----
162	2908	do	5½ miles E	4.10	.63	15.37	-----
159	2905	Foliage, black oak, uninjured.	8½ miles E	3.15	.49	15.55	-----

## SOUTH OF SMELTERS.

Field No.	Serial No.	Description of sample.	Approximate distance and direction from smelters.	Ash in leaves and needles.	Sulphur trioxid—		
					In leaves.	In ash.	In soil.
103	2849	Foliage, white oak, injured.	2 miles SSW	<i>Per cent.</i> 6.43	<i>Per cent.</i> 0.92	<i>Per cent.</i> 14.30	<i>Per cent.</i> -----
158	2904	Foliage, white oak, uninjured.	8½ miles E	4.78	.58	12.13	-----
105	2851	Soil beneath No. 103	-----	-----	-----	-----	0.05
161	2907	Soil beneath No. 158	-----	-----	-----	-----	.04
106	2852	Foliage, white oak, injured.	3 miles SSW	3.63	.49	13.49	-----
158	2904	Foliage, white oak, uninjured.	8½ miles E	4.78	.58	12.13	-----
143	2889	Foliage, shortleaf pine, injured.	3¾ miles S	2.97	.66	22.22	-----
144	2890	do	do	2.91	.50	20.61	-----
145	2891	do	do	2.83	.71	25.08	-----
157	2903	Foliage, shortleaf pine, uninjured.	8½ miles E	2.82	.40	14.18	-----
148	2894	Soil beneath Nos. 143, 144, 145.	-----	-----	-----	-----	.05
161	2907	Soil beneath No. 157	-----	-----	-----	-----	.04
138	2884	Foliage, white oak, injured.	4 miles S	5.46	1.03	18.86	-----
158	2904	Foliage, white oak, uninjured.	8½ miles E	4.78	.58	12.13	-----
142	2888	Soil beneath No. 138	-----	-----	-----	-----	.04
161	2907	Soil beneath No. 158	-----	-----	-----	-----	.04
136	2882	Foliage, white oak, injured.	6½ miles SSE	4.58	.77	16.81	-----
158	2904	Foliage, white oak, uninjured.	8½ miles E	4.78	.58	12.13	-----

TABLE II.—Sulphur trioxid in foliage, in ash, and in soils around smelters—  
Continued.

## SOUTH OF SMELTERS—Continued.

Field No.	Serial No.	Description of sample.	Approximate distance and direction from smelters.	Ash in leaves and needles.	Sulphur trioxid—		
					In leaves.	In ash.	In soil.
134	2880	Foliage, black oak, injured.	6½ miles SSE.	<i>Per cent.</i> 4.52	<i>Per cent.</i> 0.73	<i>Per cent.</i> 16.15	-----
159	2905	Foliage, black oak, uninjured.	8½ miles E.	3.15	.49	15.55	-----
120	2866	Foliage, black oak, injured.	9 miles SSW.	3.58	.39	10.89	-----
159	2905	Foliage, black oak, uninjured.	8½ miles E.	3.15	.49	15.55	-----
128	2874	Foliage, black oak, injured.	9½ miles SSE.	4.69	.63	13.43	-----
129	2879	do.	do.	4.32	.57	13.19	-----
159	2905	Foliage, black oak, uninjured.	8½ miles E.	3.15	.49	15.55	-----
131	2877	Soil beneath Nos. 128, 129.	-----	-----	-----	-----	0.05
161	2907	Soil beneath No. 159.	-----	-----	-----	-----	.04
124	2870	Foliage, scarlet oak, injured.	10½ miles S.	2.72	.67	24.62	-----
160	2906	Foliage, scarlet oak, uninjured.	8½ miles E.	2.77	.50	18.05	-----
126	2872	Foliage, black oak, injured.	10½ miles S.	3.59	.41	11.42	-----
159	2905	Foliage, black oak, uninjured.	8½ miles E.	3.15	.49	15.55	-----

## WEST OF SMELTERS.

				<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1	2747	Foliage, post oak, injured.	2½ miles WNW.	4.53	1.31	28.92	-----
3	2749	do.	3 miles WNW.	4.60	1.02	22.18	-----
5	2751	do.	do.	5.36	1.13	21.08	-----
24	2770	Foliage, post oak, uninjured.	13½ miles WNW.	5.48	.57	10.40	-----
7	2753	Foliage, white oak, injured.	3 miles WNW.	4.46	1.09	24.44	-----
25	2771	Foliage, white oak, uninjured.	13½ miles WNW.	6.11	.79	12.93	-----
9	2755	Soil beneath No. 7.	-----	-----	-----	-----	0.06
27	2773	Soil beneath No. 25.	-----	-----	-----	-----	.04
10	2756	Foliage, shortleaf pine, injured.	5 miles WNW.	3.47	.84	24.21	-----
15	2761	do.	do.	4.18	.86	20.57	-----
23	2769	Foliage, shortleaf pine, uninjured.	13½ miles WNW.	4.40	.57	12.95	-----
12	2758	Foliage, white oak, injured.	5 miles WNW.	4.47	.92	20.58	-----
25	2771	Foliage, white oak, uninjured.	13½ miles WNW.	6.11	.79	12.93	-----
14	2760	Soil beneath Nos. 10, 15, 12.	-----	-----	-----	-----	.04
27	2773	Soil beneath Nos. 23, 25.	-----	-----	-----	-----	.04
17	2763	Foliage, white pine, injured.	6 miles WNW.	2.98	.73	24.50	-----
18	2764	do.	do.	2.36	.73	30.93	-----
28	2774	Foliage, white pine, uninjured.	13½ miles WNW.	3.08	.47	15.26	-----
20	2766	Foliage, Spanish oak, injured.	6 miles WNW.	4.29	1.31	30.53	-----
26	2772	Foliage, Spanish oak, uninjured.	13½ miles WNW.	4.58	.69	15.07	-----
22	2768	Soil beneath Nos. 17, 18, 20.	-----	-----	-----	-----	.06
27	2773	Soil beneath Nos. 28, 26.	-----	-----	-----	-----	.04
180	2926	Foliage, white pine, injured.	8 miles W.	2.48	.71	28.63	-----
28	2774	Foliage, white pine, uninjured.	13½ miles WNW.	3.08	.47	15.26	-----
184	2930	Soil beneath No. 180.	-----	-----	-----	-----	.04
27	2773	Soil beneath No. 28.	-----	-----	-----	-----	.04
29	2775	Foliage, white pine, injured.	9½ miles WNW.	1.90	.54	28.42	-----
28	2774	Foliage, white pine, uninjured.	13½ miles WNW.	3.08	.47	15.26	-----



In this table, with possibly two or three exceptions, it will be noted that the soils close to the smelters contain very nearly the same amounts of sulphur trioxid as those farther away, so that in comparing injured trees situated near the smelter with uninjured trees at a greater distance the soils in which they grew may be considered identical.

Out of 49 such comparisons it will be noted that 46 times, or in 94 per cent of the cases examined, the sulphur trioxid content of the injured trees is larger than that of the uninjured trees of the same species situated beyond the range of the seemingly significant damage and that in 40 cases, or 82 per cent of the number examined, the sulphur trioxid content of the ash of such injured trees is larger than that of similar uninjured trees situated beyond the range of apparent damage.

In a northerly direction in 100 per cent of the cases examined the leaves of the injured trees contain a larger percentage of sulphur trioxid than the leaves of the uninjured trees and in 81 per cent of the examinations the ash of such injured trees contains a larger percentage of sulphur trioxid than the ash of the uninjured trees.

In an easterly direction in 100 per cent of the cases examined the leaves of the injured trees contain a larger percentage of sulphur trioxid than those of the uninjured trees and in 75 per cent of the cases examined the ash of such injured trees contains a larger percentage of sulphur trioxid than the ash of those uninjured.

In a southerly direction in 77 per cent of the cases examined the leaves of the injured trees contain a larger percentage of sulphur trioxid than the leaves of the uninjured trees and in 69 per cent of the examinations the ash of such injured trees contains a larger percentage of sulphur trioxid than the ash of those uninjured.

In a southerly direction, if only those trees are considered which were within a distance of  $6\frac{1}{2}$  miles from the smelters, it appears that in 88 per cent of the cases examined the leaves of the injured trees contain a larger percentage of sulphur trioxid than those of the uninjured trees and in 100 per cent of the examinations the ash of such injured trees contains a larger percentage of sulphur trioxid than the ash of those that are uninjured.

In a westerly direction in 100 per cent of the examinations both the leaves and the ash of the injured trees show a larger content of sulphur trioxid than do the leaves and the ash of the uninjured trees.

From this investigation the following conclusions are drawn in regard to the distribution of the injury by smelter fumes:

(1) The vegetation around the smelters appears from actual chemical analysis to be injured for at least 12 to  $12\frac{1}{2}$  miles north of the smelters,  $6\frac{1}{2}$  miles south,  $5\frac{1}{2}$  to 6 miles east, and  $9\frac{1}{2}$  miles west.

(2) There can be but little doubt that the injury extends beyond the limits mentioned in the preceding paragraph, but this can not be shown by chemical analysis, since the difference in sulphur trioxid content between injured and uninjured trees becomes so small as to be within the limits of experimental error.

### **INVESTIGATIONS OF INJURY TO VEGETATION AND ANIMAL LIFE BY SMELTER WASTES AROUND ANACONDA, MONT.**

A third extremely important study of injury to vegetation and animal life by smelter wastes was conducted by the writer in the country surrounding Anaconda, Mont., and at Washington during the latter part of 1906 and the whole of 1907. In the immediate vicinity of Anaconda the huge Washoe smelter is situated, roasting, when running at full head, from 8,000 to 10,000 tons of ore per day, which ore is said to contain quite large quantities of arsenic. (See Pl. V.)

The plant is situated in a semiarid country, where irrigation is practiced, and discharges its tailings and slags into certain of the streams that are used for irrigation purposes. There are therefore three distinct problems to be worked out in connection with the injury caused by the smelter:

(1) Whether or not the vegetation is injured by reason of the sulphur dioxid and trioxid set free.

(2) Whether enough arsenic is set free to settle on the surrounding forage plants to make them unfit for stock.

(3) Whether the waste when discharged into the irrigation streams renders the water unfit for irrigation purposes and injures the soil to which such water is applied. All of these problems were studied, and definite data bearing thereon obtained.

The chemist in this investigation was accompanied by one of the foresters of the Department of Agriculture. Samples of soil, foliage of trees, forage plants, irrigation waters, ores, and of the dump heap were collected and forwarded to the Bureau of Chemistry for chemical examination. As in the Tennessee investigation, samples of foliage were collected from those trees which the forester was certain had not died from insect pests, forest fires, crowding, or other common causes of forest destruction.

A few paragraphs of introduction are necessary in regard to the situation of the smelter and the appearance of the surrounding country.

#### **LOCATION OF SMELTER AND APPEARANCE OF SURROUNDING VEGETATION.**

The Washoe smelter is situated on a high hill toward the southern end of Deer Lodge Valley, which is about 35 miles long and from 4 to 6 miles wide. (See Pl. VI.) It is located about at the junction

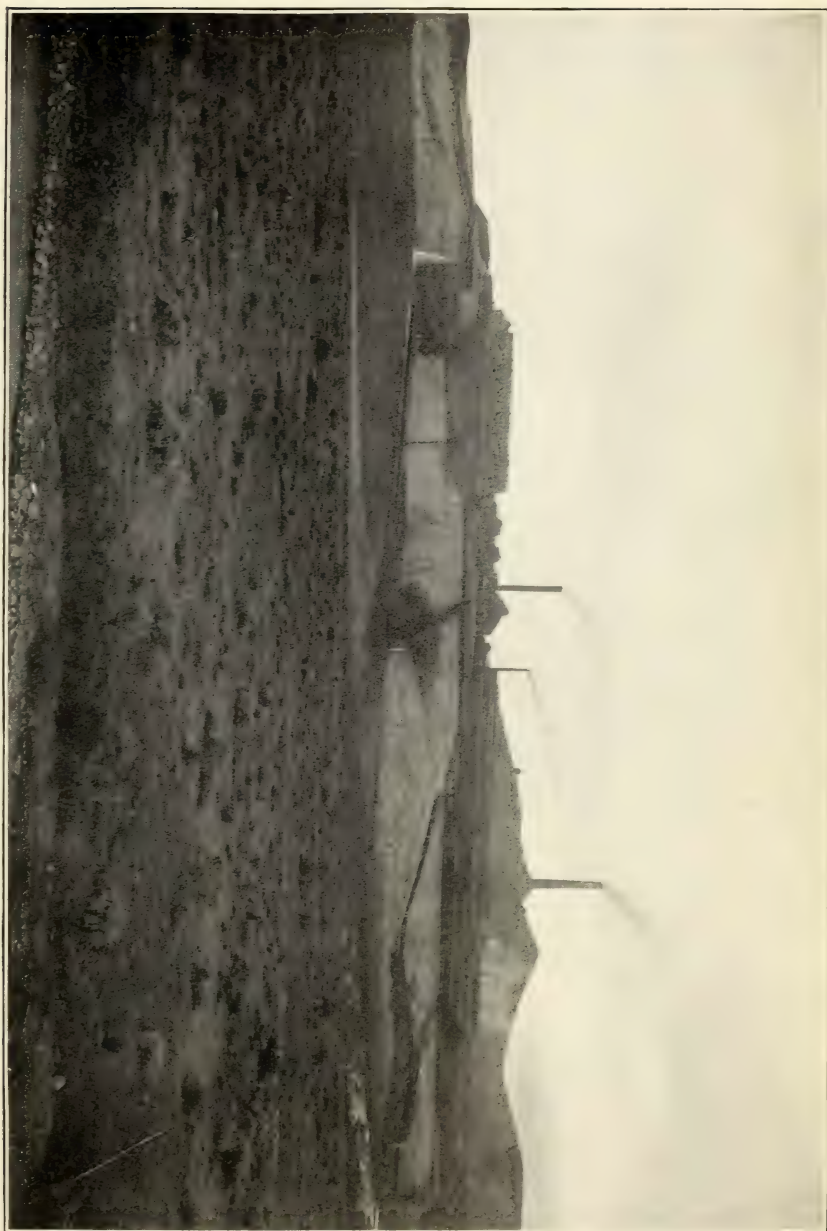
of Deer Lodge Valley and Warm Springs Creek Valley, and is near the Hell Gate and Helena National Forests and certain other public lands. To the north, south, east, and west of this valley are quite high ridges of mountains which are cleft here and there by the valleys of small creeks, of which Warm Springs Valley is one of the largest. Down the center of Deer Lodge Valley runs the river of that name, into which is carried part of the tailings and slag from the plant and the wash from the dumps and slime heaps. As before mentioned, this river is used for irrigation purposes, although a large number of the farmers say that it is injurious and prefer to get their water from small creeks coming down from the mountains on either side, only using the river water when it is absolutely necessary. It is only near the tops of ridges and beyond them and along the valleys of the various small streams that the land is forested to any extent. Besides this, forest fires have swept over certain of the mountains in the past, so that all dead timber can not be ascribed to sulphur dioxid from the smelter. However, enough trees remain within a radius of 10 to 15 miles from the smelter, which have not been injured in any way by the forest fires, crowding, insect pests, etc., to enable one to observe the damage caused by sulphur dioxid. The three principal kinds of trees in the neighborhood of the smelter are the lodgepole pine, juniper, and red fir. The difference in their resistance to sulphur dioxid fumes is very marked and can easily be observed.

Immediately surrounding the smelter practically all trees are either dead or severely injured. A very few trees still stand, to which those who do not believe in the injurious effects of smelter fumes point with pride as examples of the fact that sulphur dioxid does not injure vegetation. Since, however, hundreds of the same kinds of trees are killed outright at ten times the distance from the smelter, the force of the argument is entirely lost and the few seemingly uninjured trees near by only appear to a disinterested person as curious examples of individual resistance.

#### NORTH OF THE SMELTER.

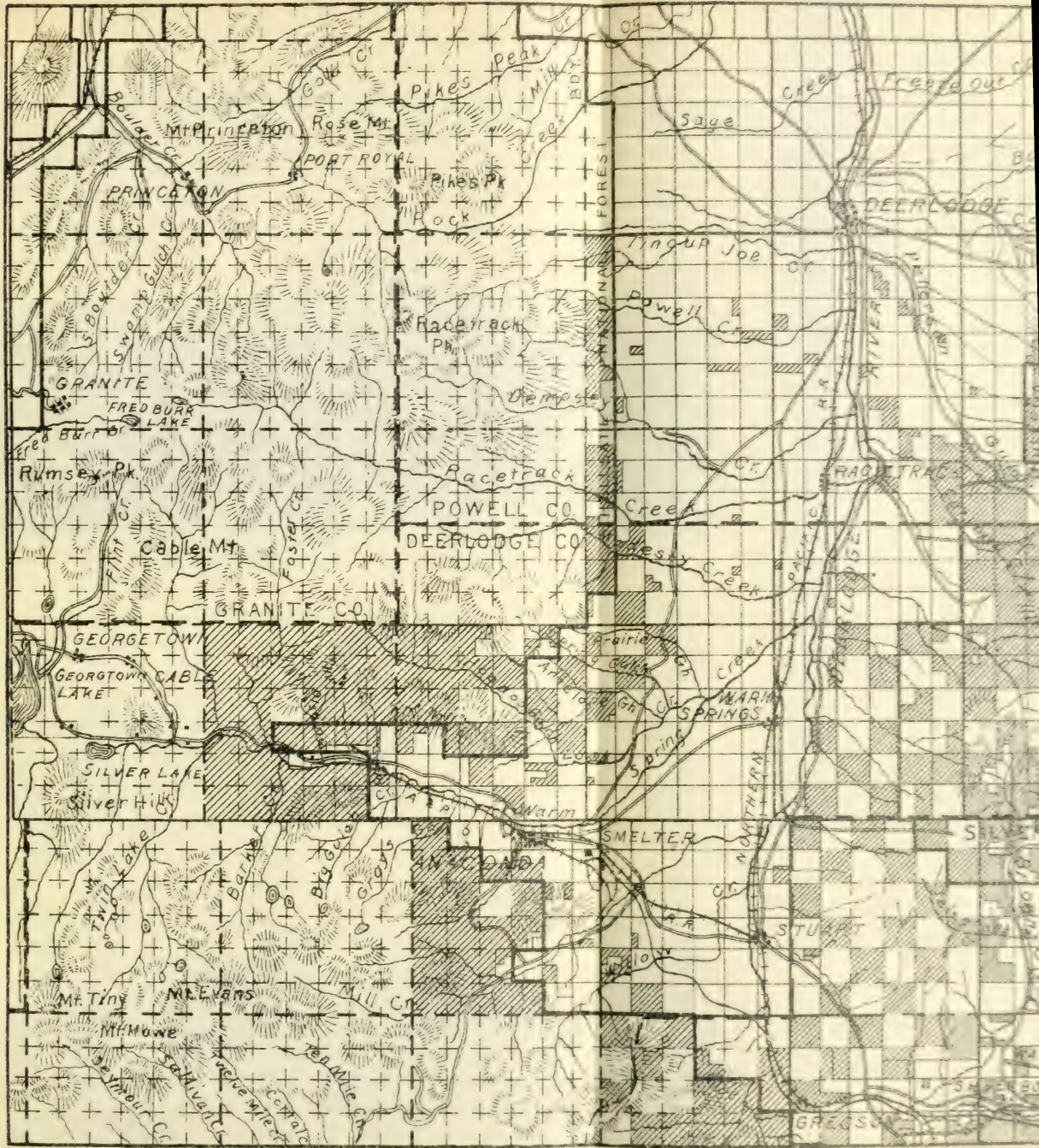
Going north from the smelter a trip was first made from Anaconda in a direction slightly east of north, until the road running along the east side of Deer Lodge River was reached. This road was followed to the vicinity of Race Track. Here the river was again crossed and the road running on the west side of the Deer Lodge River was followed as far as Deer Lodge. On the return the same route was followed, except that the trip along the east side of the river was continued farther south to a point beyond J. R. Perdee's ranch. Various samples of cattle-food materials, soils, and Deer Lodge water were collected and observations on the general appearance of the vegetation were made. It was noted that the bushes and trees along the streams





WASHOE SMELTER AT ANACONDA, MONT., IN OPERATION.





R. 13 W.

R. 12 W.

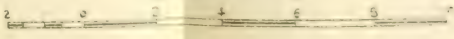
R. 11 W.

R. 10 W.

R. 9 W.

R.

SCALE IN MILES



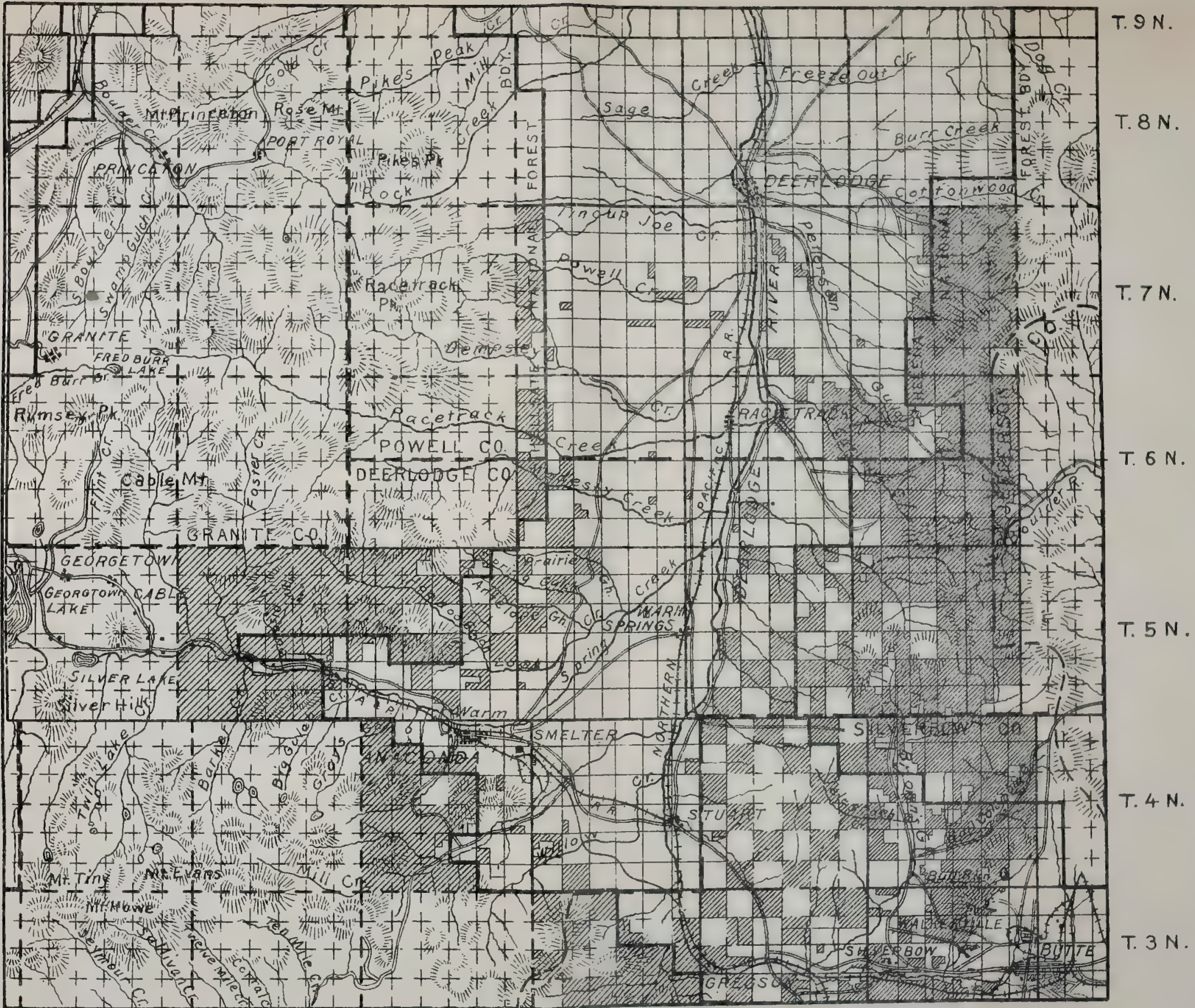
— National Forest Boundary

Public Lands

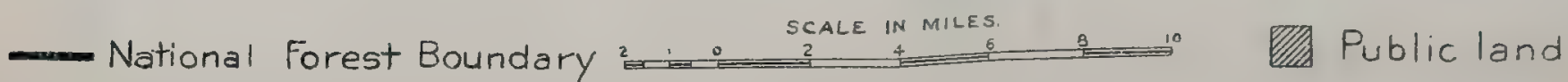








R. 13 W.      R. 12 W.      R. 11 W.      R. 10 W.      R. 9 W.      R. 8 W.      R. 7 W.



REGION AROUND ANACONDA, MONTANA, SHOWING NATIONAL FOREST BOUNDARY AND PUBLIC LANDS IN R. 8 W., R. 9 W., R. 10 W., Tps. 3, 4, 5, 6, AND 7 N. IN EACH RANGE; R. 11 W., Tps. 4 AND 5 N.; AND R. 12 W., T. 5 N.









FIG. 1.—VIEW OF MOUNTAIN ABOUT 2.5 MILES WEST FROM WASHOE SMELTER—FORMERLY COVERED WITH TIMBER TOWARD THE SUMMIT, BUT NOW BARE.



FIG. 2.—VIEW OF MOUNTAIN SIDE ABOUT 3 MILES WEST FROM WASHOE SMELTER—RED FIRS KILLED AND JUNIPERS APPARENTLY UNINJURED.





FIG. 1.—VIEW OF MOUNTAIN SIDE ABOUT 10.5 MILES WEST FROM WASHOE SMELTER—RED FIRS KILLED AND LODGEPOLE PINES INJURED.

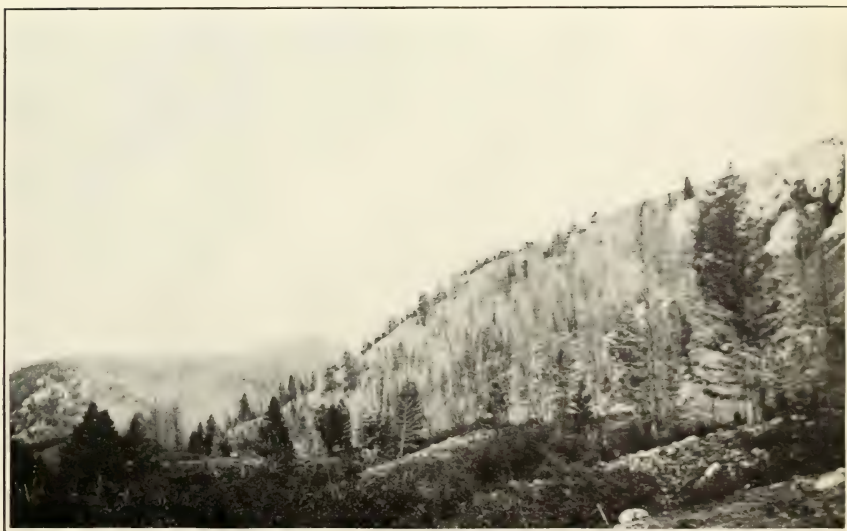


FIG. 2.—VIEW OF MOUNTAINS ABOUT 11 MILES WEST FROM WASHOE SMELTER—LIGHT AREAS ALONG MOUNTAIN SIDES SHOW PRACTICALLY TOTAL DESTRUCTION OF RED FIRS WITH NO SIGN OF RECENT FOREST FIRES.





were badly spotted and injured for several miles from the smelter, and down as far as Race Track the crops did not appear to grow as luxuriantly as those around Deer Lodge. The trees growing in the valley were so few in number that it was nearly impossible to judge what their injury might have been. In several places examined south of Race Track the soil that had been irrigated by Deer Lodge River water appeared to be injured, especially near the irrigation ditches. This injury was shown by bare spots in various fields, such spots often showing a blue-tinted crust that evidently contained copper. This was especially true in fields along the river in the vicinity of Race Track. Beyond this point no serious injury to the few trees remaining was noted. The crops of alfalfa, potatoes, clover, etc., examined beyond Race Track did not show any evidence of having been attacked by smelter fumes.

A trip was next made from Anaconda along the western side of Deer Lodge Valley until Lost Creek was reached, the valley of this creek being followed for about 7 miles. Samples of cattle-food materials, soils, and foliage were collected and observations were made on the general appearance of the vegetation. In Lost Creek Valley the junipers were absolutely uninjured, and the lodgepole pines were badly injured at the lower end of the valley, but the damage gradually grew less until it became practically insignificant at a distance of about 5 miles up the valley. Throughout the entire 7 miles of the valley the red firs were almost all killed, although an occasional live one, or a group of them, would be found.

A trip was made from Anaconda along the western side of Deer Lodge Valley until Modesty Creek was reached. The valley of this creek was followed for about 5 miles. Samples of cattle-food materials, soils, and foliage were collected and observations were made on the general appearance of the vegetation. The lodgepole pines throughout this valley were injured to only a very slight degree, this distance evidently being near the extreme limit of injury for this species of tree. About 50 per cent of the red firs were dead or badly injured and those remaining did not appear to be healthy.

Another excursion was made from Deer Lodge up the valley of Tin Cup Joe Creek for 2 or 3 miles. The lodgepole pines were uninjured and reforestation was taking place. The red firs were hardly touched, only the older ones showing any injury at all, while young red firs were rapidly springing up. On the whole it appears that this valley is beyond the limit of injury to lodgepole pines and at the extreme limit of injury to red firs.

#### EAST OF THE SMELTER.

The only trip made to the east of the smelter was in connection with the return trip from Deer Lodge, already described. As far as the writer examined east (which was to J. R. Perdee's place, a dis-

tance of about 6 miles), the few trees and crops that existed appeared to be considerably damaged. It is possible, however, that this was due partly to lack of attention on the part of the ranchers. No attempt was made to examine the mountains on the east side of the Deer Lodge Valley, as it would have been impossible to tell whether any injury that was found was due to the smelter at Anaconda, or to those in the vicinity of Butte.

#### SOUTH OF THE SMELTER.

Going south from Anaconda, a trip was made along the road which first runs to the east and then turns southwest until it crosses the divide. The point reached was 9 or 10 miles southwest of the smelter and about 2 miles beyond the divide. Samples of soils and foliage and dump and slime samples from the smelter were collected, and observations made on the general appearance of the vegetation. Three miles south of the smelter the trembling aspens were badly injured, spots appearing all over the leaves. Four miles south some of the lodgepole pines were dead, while the remainder were badly injured; practically all red firs were dead. Five miles southwest of the smelter the lodgepole pines were damaged less, but still showed injury to a considerable extent; again, the red firs were practically all dead. For from 6 to 8 miles southwest of the smelter, to the divide, the lodgepole pines were living, but most of them showed more or less injury to the ends of needles; again the red firs were nearly all dead, or seriously injured. Two miles beyond the divide the forest did not appear to be damaged.

#### WEST OF THE SMELTER.

A trip was made in a westerly direction from Anaconda up Warm Springs Creek to Silver Lake and back. Samples of cattle-food materials, soils, and foliage were gathered and observations on the general appearance of the vegetation were made. None of the junipers observed on the western trip were injured in the slightest degree. The lodgepole pines were all killed in the vicinity of the smelter, but the injury to this species gradually grew less, until, at about 10 miles west of the smelter or slightly beyond this, it ceased entirely, and beyond this point they were apparently uninjured. The damage to red firs was exceedingly great for a distance of 13 miles west, gradually growing less beyond this point, until on the shore of Silver Lake, 15 miles west of the smelter, it apparently nearly ceased. (See Pls. VII and VIII.)

On the whole it may be said that the injury to red firs around the Washoe smelter extends for a distance of about 15 to 20 miles north, an indefinite distance east, 8 miles south, and 15 miles west. The injury to lodgepole pines, however, only extends for a distance of 9 to 10 miles north, an indefinite distance east, 8 miles south, and about 10 miles west.



## SULPHUR TRIOXID IN THE FOLIAGE OF TREES AROUND WASHOE SMELTER.

The samples of injured foliage near the smelter and of uninjured foliage of the same species of trees beyond the apparent range of smoke damage, collected on the trips enumerated, were examined for sulphur trioxid and ash and the results were compared, as in the Tennessee investigation. The soils beneath the injured and uninjured trees were examined for sulphur trioxid, to determine whether any increase in the sulphur trioxid of the injured leaves could be due to an increased amount of this constituent in the soil. In the following table are given the results obtained:

TABLE III.—*Sulphur trioxid in foliage, in ash, and in soils around Washoe smelter.*

[Calculated to dry basis.]  
NORTH OF SMELTER.

Serial No.	Description of sample.	Location and approximate distance from smelter.	Ash in leaves and needles.	Sulphur trioxid—		
				In leaves.	In ash.	In soil.
			<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
4153	Foliage, injured red fir.	5 miles N, 2½ miles up Lost Creek Gulch.	4.39	1.11	25.29	.....
4879	Foliage, uninjured red fir.	18-19 miles N, 1¼ miles up Tin Cup Joe Gulch, seemingly beyond range of damage.	4.52	.84	18.53	.....
4882	do	do	4.57	.86	18.82	.....
	Average			.85	18.70	.....
4166	Soil beneath No. 4153					0.08
4883	Soil beneath No. 4879					.02
4884	Soil beneath No. 4882					.013
4154	Foliage, injured red fir.	5 miles N, 2½ miles up Lost Creek Gulch.	4.43	1.25	28.22	.....
4879	Foliage, uninjured red fir.	18-19 miles N, 1¼ miles up Tin Cup Joe Gulch, seemingly beyond range of damage.	4.52	.84	18.53	.....
4882	do	do	4.57	.86	18.82	.....
	Average			.85	18.70	.....
4166	Soil beneath No. 4154					.08
4883	Soil beneath No. 4879					.02
4884	Soil beneath No. 4882					.013
4222	Foliage, injured lodgepole pine.	10 miles N, 3 miles up Modesty Creek Gulch.	2.61	.47	18.01	.....
4877	Foliage, uninjured lodgepole pine.	18-19 miles N, 1¼ miles up Tin Cup Joe Gulch, seemingly beyond range of damage.	2.45	.49	20.00	.....
4878	do	do	2.87	.61	21.26	.....
	Average			.55	20.63	.....
4168	Soil beneath No. 4222					.02
4883	Soil beneath No. 4877					.02
	Soil beneath No. 4878					
4223	Foliage, injured lodgepole pine.	10 miles N, 3 miles up Modesty Creek Gulch.	2.82	.74	26.24	.....
4877	Foliage, uninjured lodgepole pine.	18-19 miles N, 1¼ miles up Tin Cup Joe Gulch, seemingly beyond range of damage.	2.45	.49	20.00	.....
4878	do	do	2.87	.61	21.26	.....
	Average			.55	20.63	.....

TABLE III.—Sulphur trioxid in foliage, in ash, and in soils, etc.—Continued.

## NORTH OF SMELTER—Continued.

Serial No.	Description of sample.	Location and approximate distance from smelter.	Ash in leaves and needles.	Sulphur trioxid—		
				In leaves.	In ash.	In soil.
			Per cent.	Per cent.	Per cent.	Per cent.
4168	Soil beneath No. 4223.	.....	.....	.....	.....	0.02
4883	Soil beneath No. 4877.	.....	.....	.....	.....	.02
	Soil beneath No. 4878.	.....	.....	.....	.....	.....
4225	Foliage, injured red fir.	10 miles N, 3 miles up Modesty Creek Gulch.	4.85	1.04	21.44	.....
4879	Foliage, uninjured red fir.	18-19 miles N, 1½ miles up Tin Cup Joe Gulch, seemingly beyond range of damage.	4.52	.84	18.58	.....
4882	do.....	do.....	4.57	.86	18.82	.....
	Average.....	.....	.....	.85	18.70	.....
4168	Soil beneath No. 4225.	.....	.....	.....	.....	.02
4883	Soil beneath No. 4879.	.....	.....	.....	.....	.02
4884	Soil beneath No. 4882.	.....	.....	.....	.....	.013
4226	Foliage, injured red fir.	10 miles N, 3 miles up Modesty Creek Gulch.	4.73	.90	19.03	.....
4879	Foliage, uninjured red fir.	18-19 miles N, 1½ miles up Tin Cup Joe Gulch, seemingly beyond range of damage.	4.52	.84	18.58	.....
4882	do.....	do.....	4.57	.86	18.82	.....
	Average.....	.....	.....	.85	18.70	.....
4168	Soil beneath No. 4226.	.....	.....	.....	.....	.02
4883	Soil beneath No. 4879.	.....	.....	.....	.....	.02
4884	Soil beneath No. 4882.	.....	.....	.....	.....	.013

## SOUTH OF SMELTER.

			Per cent.	Per cent.	Per cent.	Per cent.
4070	Foliage, injured lodgepole pine.	4 to 4½ miles a little W of S..	3.17	0.95	30.00	.....
4080	Foliage, uninjured lodgepole pines.	10 miles SW; 2 miles beyond divide, seemingly beyond range of damage.	2.68	.51	19.03	.....
4081			2.69	.73	27.14	.....
	Average.....	.....	.....	.62	23.09	.....
4161	Soil beneath No. 4070.	.....	.....	.....	.....	.....
4163	Soil beneath No. 4080.	.....	.....	.....	.....	0.03
	Soil beneath No. 4081.	.....	.....	.....	.....	.02
4071	Injured lodgepole pine	4 to 4½ miles W of S.....	2.69	.76	28.25	.....
4080	Foliage, uninjured lodgepole pines.	10 miles SW; 2 miles beyond divide, seemingly beyond range of damage.	2.68	.51	19.03	.....
4081			2.69	.73	27.14	.....
	Average.....	.....	.....	.62	23.09	.....
4161	Soil beneath, No. 4071.	.....	.....	.....	.....	.03
4163	Soil beneath No. 4080.	.....	.....	.....	.....	.02
	Soil beneath No. 4081.	.....	.....	.....	.....	.....
4074	Foliage, injured lodgepole pine.	5 miles SW.....	3.51	.82	23.36	.....
4080	Foliage, uninjured lodgepole pines.	10 miles SW; 2 miles beyond divide, seemingly beyond range of damage.	2.68	.51	19.03	.....
4081			2.69	.73	27.14	.....
	Average.....	.....	.....	.62	23.09	.....
4162	Soil beneath No. 4074.	.....	.....	.....	.....	.02
4163	Soil beneath No. 4080.	.....	.....	.....	.....	.02
	Soil beneath No. 4081.	.....	.....	.....	.....	.....
4075	Foliage, injured lodgepole pine.	5 miles SW.....	3.43	1.02	29.74	.....
4080	Foliage, uninjured lodgepole pines.	10 miles SW; 2 miles beyond divide, seemingly beyond range of damage.	2.68	.51	19.03	.....
4081			2.69	.73	27.14	.....
	Average.....	.....	.....	.62	23.09	.....

TABLE III.—*Sulphur trioxid in foliage, in ash, and in soils, etc.*—Continued.

## SOUTH OF SMELTER—Continued.

Serial No.	Description of sample.	Location and approximate distance from smelter.	Ash in leaves and needles.	Sulphur trioxid—		
				In leaves.	In ash.	In soil.
			<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
4162	Soil beneath No. 4075.					0.02
4163	{ Soil beneath No. 4080. Soil beneath No. 4081.					.02
4077	Foliage, injured lodgepole pine.	6 miles SW	2.53	0.90	35.57	
4080	Foliage, uninjured lodgepole pines.	10 miles SW; 2 miles beyond divide, seemingly beyond range of damage.	2.68	.51	19.03	
4081			2.69	.73	27.14	
	Average			.62	23.09	
	{ Soil beneath No. 4077. Soil beneath No. 4080. Soil beneath No. 4081.					
4078	Foliage, injured lodgepole pine.	6 miles SW	2.54	.59	23.23	
4080	Foliage, uninjured lodgepole pines.	10 miles SW; 2 miles beyond divide, seemingly beyond range of damage.	2.68	.51	19.03	
4081			2.69	.73	27.14	
	Average			.62	23.09	
	{ Soil beneath No. 4078. Soil beneath No. 4080. Soil beneath No. 4081.					

## WEST OF SMELTER.

			<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
4089	Foliage, injured lodgepole pine.	6 miles W	2.91	0.75	25.77	
4152	Foliage, uninjured lodgepole pine.	15 miles W; shore of Silver Lake, seemingly beyond range of damage.	2.61	.30	11.49	
	{ Soil beneath No. 4089. Soil beneath No. 4152.					
4089	Foliage, injured lodgepole pine.	6 miles W	2.68	.69	25.75	
4152	Foliage, uninjured lodgepole pine.	15 miles W; shore of Silver Lake, seemingly beyond range of damage.	2.61	.30	11.49	
	{ Soil beneath No. 4090. Soil beneath No. 4152.					
4086	Foliage, injured lodgepole pine.	7 miles W	3.15	.53	16.83	
4152	Foliage, uninjured lodgepole pine.	15 miles W; shore of Silver Lake, seemingly beyond range of damage.	2.61	.30	11.49	
4167	Soil beneath No. 4086.					0.02
4165	Soil beneath No. 4152.					.02
4087	Foliage, injured lodgepole pine.	7 miles W	2.91	.68	23.37	
4152	Foliage, uninjured lodgepole pine.	15 miles W; shore of Silver Lake, seemingly beyond range of damage.	2.61	.30	11.49	
4167	Soil beneath No. 4087.					.02
4165	Soil beneath No. 4152.					.02
4082	Foliage, injured red fir.	11 miles W	5.53	1.30	23.51	
4084	Foliage, uninjured red fir.	15 miles W; shore of Silver Lake, seemingly beyond range of damage.	5.56	.82	14.75	
4164	Soil beneath No. 4082.					.02
4165	Soil beneath No. 4084.					.02
4085	Foliage, injured red fir.	13 miles W	4.50	1.03	22.89	
4084	Foliage, uninjured red fir.	15 miles W; shore of Silver Lake, seemingly beyond range of damage.	5.56	.82	14.75	
	{ Soil beneath No. 4085. Soil beneath No. 4084.					



In the preceding table, with possibly two exceptions, the soils near the smelter contain practically the same amount of sulphur trioxid as the soils farther away, apparently beyond the range of smoke damage, so that in comparing injured with uninjured trees, the soils in which they grew need not be considered as a factor.

Of 18 comparisons of injured and uninjured trees it will be noted that in 16 cases, or in 89 per cent of the examinations made, the sulphur trioxid content of the injured trees is larger than that of the individual uninjured trees, and also exceeds the averages for the uninjured trees of the same species situated beyond the range of significant damage. In 17 cases, or 94 per cent of the examinations, the sulphur trioxid content of the ash of such injured trees is larger than the average sulphur trioxid content of the ash of similar uninjured trees situated beyond the range of significant damage. In only 15 cases (83 per cent of those examined), however, is the sulphur trioxid content of the ash of such injured trees larger than both the sulphur trioxid content of the ash of the individual uninjured trees and the averages for the same.

In a northerly direction, in 83 per cent of the cases examined, both the leaves and ash of the injured trees contain a larger percentage of sulphur trioxid than the leaves and ash of the uninjured trees, both as regards individual and average data.

In a southerly direction, in 83 per cent of the cases examined, the leaves of the injured trees contain a larger percentage of sulphur trioxid than the leaves of uninjured trees, and in 100 per cent of the cases the ash of such injured trees contains a larger percentage of sulphur trioxid than the average ash for the uninjured trees. In only 67 per cent of the cases examined, however, does the ash of the injured trees contain a larger percentage of sulphur trioxid than that of both the individual uninjured trees and the averages for the uninjured trees.

In a westerly direction, in 100 per cent of the cases examined, both the leaves and ash of the injured trees contain a larger percentage of sulphur trioxid than the leaves and ash of uninjured trees.

Since the above discussion shows that the trees around the Washoe smelter are evidently injured by sulphur dioxid, it becomes necessary to prove that this compound is given off from the smelter. Several samples of ore from mines that supply the smelter were examined and the following amounts of sulphur were found:

TABLE IV.—*Sulphur content of ore samples.*

Serial No.	Name of mine furnishing ore.	Sulphur.	Serial No.	Name of mine furnishing ore.	Sulphur.
		<i>Per cent.</i>			<i>Per cent.</i>
4258-----	Speculator-----	27.50	4261-----	Never Sweat-----	20.83
4263-----	do-----	19.77	4262-----	Diamond-----	24.31
4259-----	Parrot-----	28.32	4264-----	Anaconda-----	29.85
4260-----	do-----	22.18			

It is a matter of general knowledge that a large percentage of the sulphur in the ore is given off as sulphur dioxide in the usual smelter operations. If the ores given in Table IV are fairly representative samples of the material smelted at Anaconda, and if 8,000 tons of ore are handled each day, it will at once be seen that a tremendous quantity of sulphur dioxide is discharged into the atmosphere. Harkins and Swain<sup>a</sup> have studied the composition of the smelter smoke from the Washoe smelter and found that the average amount of sulphur dioxide and trioxide given off per day is 4,636,000 pounds and 447,600 pounds, respectively. Unfortunately these authors do not give the composition and quantity of the ore smelted during the time that the experiments were made, so that it is impossible to calculate what percentage of the sulphur present in the original ore was discharged through the stack as sulphur dioxide and trioxide.

#### INJURY TO CATTLE BY ARSENIC IN THE VICINITY OF THE WASHOE SMELTER.

A claim made by the farmers, which required investigation, was that enough arsenic is given off from the smelter to settle on the surrounding forage crops and so poison the cattle. To determine this it is first necessary to show that the ores reduced at the smelter contain arsenic. Examinations of several samples of ore from mines which partly supply the smelter gave the following results:

TABLE V.—Arsenic content of ore samples.

Serial No.	Name of mine furnishing ore.	Metallic arsenic.	Serial No.	Name of mine furnishing ore.	Metallic arsenic.
		<i>Per cent.</i>			<i>Per cent.</i>
4258	Speculator	12.95	4261	Never Sweat	0.45
4263	do	2.54	4262	Diamond	1.17
4259	Parrot	.51	4264	Anaconda	None.
4260	do	.45			

If we reject the first sample in Table V as exceptional and consider the other ores as representative of those received at the Washoe smelter, it will be seen that such ores contain 0.85 per cent of arsenic. At this rate, if 8,000 tons of ores per day are smelted, 68 tons of arsenic enter the plant each day and, according to the officers of the smelter, only 2 tons of white arsenic are recovered daily. This, of course, does not mean 2 tons of metallic arsenic, but for convenience in discussion, it will be considered as such. There remain, therefore, 66 tons of arsenic to account for, which can only escape in a volatile form in the fumes, or be carried off in the tailings and slag. A determination of arsenic was made in two samples taken from the dump in which 0.11 and 0.07 per cent were found, or an average of

<sup>a</sup> J. Amer. Chem. Soc., 1907, 29: 970.

0.09 per cent. It is evident that the amount found in the dump can not account for the 66 tons of arsenic that go to waste; hence a considerable quantity must be volatilized. According to the investigations of Harkins and Swain, previously mentioned, the average amount of arsenic trioxid thrown off in the smoke during twenty-four hours is 59,270 pounds. Here again, however, as in the case of the sulphur compounds, the quantity of ore used was not given.

It is next necessary to show whether or not the escaping arsenic settles on the surrounding forage crops in large enough amounts to be injurious to cattle. For this purpose 20 samples of range grass and such cultivated crops as alfalfa were collected at distances varying from 1 to 10 miles from the smelter in various directions, but more especially down the Deer Lodge Valley. These samples were examined for total and soluble arsenic. The results obtained, calculated to a dry basis and expressed both as milligrams of arsenious oxid per gram of sample and grains of arsenious oxid per daily ration of 25 pounds, are given in Table VI.

TABLE VI.—*Arsenic content of forage expressed as arsenious oxid.*

[Calculated to dry basis.]

Serial No.	Description of sample.	Approximate distance and direction from smelter.	Arsenious oxid per gram of dry sample.	Arsenious oxid per 25 pounds avoirdupois of dry ration.	Water-soluble arsenious oxid per gram of dry sample.	Water-soluble arsenious oxid per 25 pounds avoirdupois of dry ration.
			Milligram.	Grains.	Milligram.	Grains.
4114	Bunch grass	2 miles N	0.103	18.0	0.683	14.5
4106	Alfalfa <sup>a</sup>	2½ miles N	.069	12.1	.041	7.2
4115	Pasture grass	3 miles N	.069	12.1	.028	4.9
4117	Range grass	do.	.054	9.5	.034	6.0
4116	Pasture grass	4 miles N., Lost Creek.	.041	7.2	.020	3.5
4107	Red top	4 miles NE	.028	4.9	.014	2.5
4118	Clover	do.	.054	9.5	.028	4.9
4119	Range grass	do.	.090	15.8	.020	3.5
4120	Alfalfa and clover (just cut).	4½ miles NE	.054	9.5	.020	3.5
4108	Red top <sup>a</sup>	5 miles NE	.055	9.6	.028	4.9
4121	Range grass	do.	.090	15.8	.069	12.1
4122	do.	6 miles NE	.104	18.2	.041	7.2
4123	do.	8 miles NE	.055	9.6	.028	4.9
4109	Alfalfa	10 miles NE	.070	12.3	.042	7.4
4124	Red top	1 mile SE	.069	12.1	.041	7.2
4112	Bunch grass	3 miles E	.042	7.4	.020	3.5
4110	Field grass <sup>a</sup>	6 miles E	.055	9.6	.041	7.2
4111	Hay <sup>a</sup>	do.	.041	7.2	.028	4.9
4125	Range grass	4 miles W	.055	9.6	.028	4.9
4113	Bunch grass	6½ miles W	.055	9.6	.028	4.9

<sup>a</sup> Supposed to have killed cattle.

From this table it is seen that arsenic was found in considerable quantities in every sample examined. In order that the cattle in this region may live at all it is evident that they must become confirmed arsenic eaters. Through the courtesy of Dr. D. E. Salmon the writer was able to examine microscopic sections and gross specimens of the viscera of a number of cattle that it was thought had been killed



by eating forage containing arsenic. It was noted that the gastrointestinal tract was inflamed and sections of the glands of the stomach and kidneys showed a desquamation of the epithelium, cloudy swelling, and in some cases fatty degeneration. The symptoms described by the farmers include inflammation of the mucous membrane of the upper air passages, running from the nose, diarrhea, thirst, emaciation, and incoordination of gait. From the above symptoms and post-mortem appearances, together with the amount of arsenic found in the various forage plants, there can be but little doubt that the cattle were killed by arsenic.<sup>a</sup>

To give some idea of the distribution of arsenic on the soil in the vicinity of the smelter, samples were taken to a depth of 2 inches at varying distances from the plant. Since it might be claimed that any arsenic found in these samples was naturally present in the soil and did not come from the smelter fumes, similar samples beyond the apparent range of the smelter smoke were also taken and examined for arsenic. The results obtained are given in Table VII.

TABLE VII.—Arsenic content of surface two inches of soils, expressed as metallic arsenic.

[Calculated to dry basis.]

Serial No.	Approximate distance and direction from smelter.	Arsenic per gram of dry soil.	Arsenic in surface two inches <sup>a</sup> of soil per square foot.	Serial No.	Approximate distance and direction from smelter.	Arsenic per gram of dry soil.	Arsenic in surface two inches <sup>a</sup> of soil per square foot.
		<i>Milligram.</i>	<i>Grains.</i>			<i>Milligram.</i>	<i>Grains.</i>
4176	2 miles N	0.50	40.2	4179	3 miles E	0.20	16.1
4169	3 miles N	.30	24.1	4170	6 miles E	.08	6.4
4171	do	.50	40.2	4177	do	.08	6.4
4173	4 miles NE	.20	16.1	4181	4 miles W	.30	24.1
4180	5 miles NE	.30	24.1	4175	6½ miles W	.25	20.1
4174	6 miles NE	.30	24.1	4165	15 miles W	None.	None.
4178	8 miles NE	.08	6.4	4163	10 miles SW	None.	None.
4172	1 mile SE	.50	40.2				

<sup>a</sup> Calculated on the basis of 69 pounds as the average weight of a cubic foot of surface soil.

From this table it is evident that the surface 2 inches of all soils examined in the vicinity of the smelter, at distances varying from 1 to 8 miles, contain large amounts of arsenic. It is also shown that this arsenic must come from the smelter, since the two soil samples taken beyond the apparent range of smelter smoke do not contain any arsenic.

<sup>a</sup> One of the pathologists of the Bureau of Animal Industry, U. S. Department of Agriculture, made a very thorough study of the post-mortem appearance of cattle in this region, and will give the results of his work in the near future.

## INJURY TO CROPS AND SOIL BY TAILINGS AND SLAG FROM THE WASHOE REDUCTION PLANT.

The third question calling for investigation was whether the water from Deer Lodge River, when used for irrigation purposes, has an injurious effect on the crops and the soil. It is evident from an inspection of this stream that tremendous quantities of waste matter from the plant find their way into it. It is also evident from the method of operation that these waste products must contain some copper which is, to a large extent, present as finely divided copper sulphid, which is known to form soluble copper sulphate naturally by gradual oxidation. It would be expected, therefore, that if this material were deposited on the land it would gradually oxidize to a soluble form, in which condition even very minute quantities of it would be more or less injurious to vegetation. It has been urged that even if soluble copper were found in the Deer Lodge River and subsequently on the land it would be immediately rendered insoluble again by the action of carbonates and bicarbonates present in the water and soil. On the surface this seems plausible. Skinner,<sup>a</sup> however, has shown that such is not the case, as when soluble copper salts are brought in contact with solutions containing carbonates and bicarbonates, enough copper still remains in solution to be toxic to plants.

Samples of the waste water from the plant, and samples from the Deer Lodge River just below where the waste flows into it, and at various distances farther down, were taken and the insoluble copper present was determined with the following results:

TABLE VIII.—Copper content of irrigation water samples.

Serial No.	Location and approximate distance from smelter.	Insoluble copper.	Soluble copper.
		Parts per million.	Parts per million.
4246	Waste water of smelter	31.0	0.05
4244	Deer Lodge River, 1½ miles below entrance of smelter water	12.1	.77
4240	Deer Lodge River, 6 miles below entrance of smelter water	12.0	.15
4241	Deer Lodge River, 8 miles below entrance of smelter water	6.4	.22
4242	Deer Lodge River, 10 miles below entrance of smelter water	6.6	Trace.
4243	Deer Lodge River at Deer Lodge, about 16-18 miles below entrance of smelter water	3.1	.51

It is evident from Table VIII that the plant discharges large quantities of copper into the Deer Lodge River and that, even at a distance of 16 to 18 miles below the point where the tailings are discharged, a considerable quantity of copper is still present.

It has been proven by Heald<sup>b</sup> that seedlings of the ordinary garden plant *Pisum sativum* are killed by the solution containing 1 part of copper in 404,423 parts of water and that Indian corn (*Zea mays*)

<sup>a</sup> Copper Salts in Irrigation Waters, J. Amer. Chem. Soc., 1906, 28: 361.

<sup>b</sup> Bot. Gaz., 1896, 22: 125.

seedlings are killed in a solution containing 1 part of copper per 808,846 parts of water. Johnson, in his work entitled *How Crops Grow*, says: "The soluble compounds of copper, arsenic, and lead are very injurious to plant life, unless very highly diluted." Other plant physiologists in their works confirm Johnson's statement. Harter<sup>a</sup> says: "In the case of many plants one of the most toxic substances known is copper, and it is more than likely that it is present in much of the water which experimenters have found to be injurious. Coupin states that one part of copper to 700,000,000 of water is sufficient to retard the root growth of wheat seedlings. A mere trace of copper is sufficient to retard growth in many cases."

The writer is now conducting some experiments to determine what amount of soluble copper in soils is injurious to the growth of certain plants. The work has not yet been completed, but the preliminary data indicate that the growth of wheat and rye is interfered with by the presence of 2.1 parts of soluble copper per million parts of earth in one soil and by 3.5 parts of soluble copper per million parts of earth in another soil.

It would appear, therefore, from these data that the Deer Lodge River, even at a distance of 16 to 18 miles below where the tailings are discharged, is not fit for irrigation purposes, and will eventually, if not at once, seriously injure land to which it is applied.

It has been suggested that the Deer Lodge River already contained so large a quantity of alkali salts that it was injurious to soil and crops, even if the smelter wastes were not present. To determine this question, a sample of the water was subjected to an irrigation-water analysis with the following results:

TABLE IX.—*Composition of Deer Lodge River water (Serial No. 4244) about 1.5 miles below where smelter waste enters.*

Determinations.		Hypothetical combination.	
	<i>Parts per million.</i>		<i>Parts per million.</i>
Bicarbonic acid ion.....	78.73	Calcium bicarbonate.....	104.59
Sulphuric acid ion.....	222.27	Calcium sulphate.....	138.00
Chlorin.....	19.00	Magnesium sulphate.....	97.34
Carbonic acid ion.....	None.	Sodium sulphate.....	69.93
Calcium.....	66.49	Sodium chlorid.....	31.35
Magnesium.....	19.69		
Sodium.....	35.03		
Total.....	441.21	Total.....	441.21

This analysis shows that the Deer Lodge River does not contain such a quantity of alkali salts as would render it unfit for irrigation purposes.

<sup>a</sup> The Variability of Wheat Varieties in Resistance to Toxic Salts. U. S. Dept. Agr., Bureau of Plant Industry, Bulletin 79, p. 40.



To further prove that the Deer Lodge River water when applied to the land adds excessive amounts of copper thereto, the soil irrigated by said water was sampled at various distances from the smelter to determine both the soluble and insoluble copper present. To further demonstrate that any large amount of copper found was not naturally present in the soil, samples not irrigated by the Deer Lodge River and not exposed to the action of the flue dust (Nos. 4163 and 4165) were also subjected to analysis. Following are the results obtained by the examination of the samples gathered in the summer of 1906:

TABLE X.—*Copper content of surface foot of soils collected in 1906.*

[Calculated to dry basis.]

Serial No.	Origin and description of sample.	Insoluble copper.	Soluble copper.
		<i>Parts per million.</i>	<i>Parts per million.</i>
4185----	8½ miles NE of smelter; irrigated by Deer Lodge River.....	1,549.4	20.4
4183----	9½ miles NE of smelter; irrigated 12 years by Deer Lodge River..	458.4	3.4
4184----	12 miles NE of smelter; irrigated by Deer Lodge River.....	1,451.6	118.2
4182----	12 miles NE of smelter; irrigated by Deer Lodge River.....	2,790.8	118.2
4186----	14 miles NE of smelter; irrigated 16 years by Deer Lodge River..	870.4	7.1
4165----	15 miles W of smelter; not irrigated by Deer Lodge River.....	Trace.	None.
4163----	10 miles SW of smelter and about 2 miles beyond divide; not irrigated by Deer Lodge River.....	13.0	Trace.

It is evident from the preceding table and what has been said of the action of copper on plants that the soils irrigated from the Deer Lodge River contain very large quantities of copper, enough of which is in a soluble condition to interfere seriously with the growth of many forms of vegetation. It is also evident that the soils beyond the range of flue dust and not irrigated by Deer Lodge River water contain very small quantities of copper, practically none of which is in a soluble condition.

The analyses given in Table X show such excessive amounts of copper in the soils irrigated by Deer Lodge River water that the writer was not willing to publish the results until they had been confirmed by collecting and examining new samples. The results given in Table XI were obtained on samples collected in 1907.

TABLE XI.—*Copper content of surface foot of soils collected in 1907.*

[Calculated to dry basis.]

Serial No.	Origin and description of sample.	Insoluble copper.	Soluble copper.
		<i>Parts per million.</i>	<i>Parts per million.</i>
4871----	8 miles NE of smelter; flooded by Deer Lodge River; no sample taken from this field in 1906.....	10,018.9	1.1
4872----	8½ miles NE of smelter; irrigated by Deer Lodge River; sample from same field (No. 4185) taken in 1906.....	979.9	1.1
4873----	9½ miles NE of smelter; irrigated twelve years by Deer Lodge River; sample from same field (No. 4183) taken in 1906.....	312.9	2.1
4874----	12 miles NE of smelter; irrigated by Deer Lodge River; sample from same field (No. 4184) taken in 1906.....	98.7	2.1
4875----	12 miles NE of smelter; irrigated by Deer Lodge River; sample from same field (No. 4182) taken in 1906.....	624.6	10.4
4876----	14 miles NE of smelter; irrigated sixteen years by Deer Lodge River; sample from same field (No. 4186) taken in 1906.....	739.8	5.2

While this table does not give the same results for either total or soluble copper as were obtained in 1906, it does show that all of these soils contain very large quantities of copper, enough of which is present in a soluble form to be dangerous to, if not prohibitive of, many forms of plant growth. It would hardly be expected that the results obtained on copper, either soluble or insoluble, would be the same for any two years, since it is very unevenly distributed over the field and furthermore is constantly changing in its proportions according to the rainfall, irrigation, amount of oxidation, season, etc. It would only be expected that any two years would show the same general condition, and this is what these analyses show.

It has been suggested that the soils irrigated by the Deer Lodge River are already so alkaline that they are unfit for growing crops, and therefore the addition of copper to the soil can not make matters worse. To test this point the samples of soils collected in 1906 were examined for the soluble salts usually present in alkali land and a determination of black alkali was made by the Skinner <sup>a</sup> method with the following results:

TABLE XII.—*Soluble salt content of surface foot of soils irrigated by Deer Lodge River.*

[Calculated to dry basis.]

ACTUAL DETERMINATIONS.

Constituents.	No. 4182: 12 miles NE of smelter.	No. 4183: 9½ miles NE of smelter.	No. 4184: 12 miles NE of smelter.	No. 4185: 8½ miles NE of smelter.	No. 4185: 14 miles NE of smelter.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Bicarbonic acid ion.....	0.034	0.101	0.018	0.165	0.107
Sulphuric acid ion.....	.355	.027	.197	.822	.031
Chlorin.....	.005	.028	.005	.030	.006
Carbonic acid ion.....	None.	None.	None.	None.	None.
Calcium.....	.100	.048	.050	.215	.034
Magnesium.....	.029	.012	.012	.079	.0095
Sodium.....	.016	.....	.025	.113	.002
Total.....	.539	.216	.307	1.494	.190

HYPOTHETICAL COMBINATION.

Calcium bicarbonate.....	0.045	0.134	0.024	0.219	0.137
Magnesium bicarbonate.....	.....	.....	.....	.....	.005
Calcium sulphate.....	.303	.038	.149	.547	.....
Magnesium sulphate.....	.143	.....	.059	.390	.039
Calcium chlorid.....	.....	.011	.....	.....	.....
Magnesium chlorid.....	.....	.029	.....	.....	.002
Sodium sulphate.....	.040	.....	.067	.283	.....
Sodium chlorid.....	.008	.....	.008	.049	.007
Total.....	.539	.212	.307	1.494	.190
Black alkali.....	None.	None.	None.	None.	None.

From these results it is evident that none of the soil samples examined contains any black alkali or a sufficient amount of white alkali to be injurious to ordinary farm crops.

From all the work done in the vicinity of Anaconda the following definite conclusions can be drawn:

(1) The forests around the smelter appear from actual chemical analysis to be injured for at least 10 miles north of the smelter, 6 miles south of the smelter, and 13 miles west of the smelter.

(2) This injury to forests by sulphur dioxide undoubtedly extends to a distance of 15 to 20 miles north of the smelter, 8 miles south of the smelter, 15 miles west of the smelter, and perhaps even farther in certain localities, although not proved by chemical analysis.

(3) The junipers are very resistant to smelter fumes and are able to grow close to the smelter; the red firs are susceptible to the fumes and are badly damaged at distances of about 15 miles or perhaps even farther; the lodgepole pines are intermediate between the other two species of trees, but show damage for at least 10 miles.

(4) Large quantities of arsenic are discharged from the smelter on the surrounding country, this poison being found in forage crops in large enough quantities to poison cattle.

(5) The waste from the reduction plant discharged into the Deer Lodge River renders it unfit for irrigation purposes.

(6) The land irrigated by the Deer Lodge River, containing the waste from the reduction plant, is greatly injured by the copper present in the irrigation water.

(7) The soils irrigated by the Deer Lodge River which were studied by the writer do not contain enough alkali salts to be injurious to ordinary farm crops.

## METHODS OF ANALYSIS USED IN INVESTIGATIONS.

### FOLIAGE OF TREES.

#### *Moisture.<sup>a</sup>*

Dry a convenient quantity (about 2 grams) of the substance in the boiling-water bath until the material ceases to lose weight.

#### *Ash.<sup>a</sup>*

Char a convenient quantity of the substance, representing about 2 grams, at the lowest possible heat. Exhaust the charred mass with water, collect the insoluble residue on a filter, burn till the ash is white or nearly so, and then add the filtrate to the ash and evaporate to dryness. Heat the whole to low redness and weigh.

#### *Sulphur trioxide.<sup>a</sup>*

Place from 1.50 to 2.50 grams of material in a nickel crucible of about 100 cc capacity and moisten with approximately 2 cc of water. Mix thoroughly, using a nickel or platinum rod. Add 5 grams of pure anhydrous sodium car-

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<sup>a</sup> Official and Provisional Methods of Analysis, U. S. Dept. Agr., Bureau of Chemistry, Bul. 107.



bonate and mix. Add pure sodium peroxid (approximately 0.5 gram) small amounts at a time, thoroughly mixing the charge after each addition. Continue adding the peroxid until the mixture becomes nearly dry and quite granular, requiring usually about 5 grams of peroxid. Place the crucible over a low alcohol flame (or other flame free from sulphur) and carefully heat, with occasional stirring, until the contents are fused. (Should the material ignite the determination is worthless.) After fusion remove the crucible, allow to cool somewhat, and cover the hardened mass with peroxid to a depth of about 0.5 cm. Heat gradually and finally with a full flame until complete fusion takes place, rotating the crucible from time to time in order to bring any particles adhering to the sides into contact with the oxidizing material. Allow to remain over the lamp for ten minutes after fusion is complete. Cool somewhat, place the warm crucible and contents in a 600 cc beaker and carefully add about 100 cc of water. After violent action has ceased, wash material out of crucible, make slightly acid with hydrochloric acid, and filter. Determine sulphates by precipitating with barium chlorid in the ordinary way.

### SOILS.

#### *Moisture.*<sup>a</sup>

Dry two or more grams in a tared platinum dish for five hours at the temperature of boiling water; cover the dish, cool in a desiccator and weigh. Repeat heating, cooling, and weighing at intervals of two hours, until the material ceases to lose weight. Weigh rapidly to avoid absorption of moisture from the air. The loss of weight is reported as moisture.

#### *Sulphur trioxid.*<sup>a</sup>

Digest 10 grams of soil on the steam bath for ten hours with 100 cc of hydrochloric acid (sp. gr. 1.115), shaking the flask every hour. Carry on this digestion in an Erlenmeyer flask, provided with ground-glass stopper ending in a reflux tube 20 inches or more in length. Remove from the bath and allow to settle. Decant the solution into a porcelain dish, wash the insoluble residue onto a filter with hot water and continue the washing until free of chlorids. Add the washings to the original solution, oxidize with a little nitric acid and evaporate to dryness on a water bath. Take up with hot water and a few cubic centimeters of hydrochloric acid and again evaporate to dryness. Again add water and sufficient hydrochloric acid to effect solution, warm and filter, washing until free from chlorids. Again evaporate this filtrate to dryness, take up with a little hydrochloric acid and water, and filter to a volume of 500 cc. Take 200 cc of the above solution for analysis, evaporate nearly to dryness to expel the excess of acid, dilute with distilled water, heat to boiling, and precipitate by means of barium chlorid. Boil for about five minutes, allow to stand in a warm place over night, filter, and determine the sulphur trioxid as barium sulphate.

#### *Arsenic.*

Weigh 1 gram of soil and treat with 25 cc of concentrated arsenic-free nitric acid in a small porcelain evaporating dish. Cover with a watch glass and digest on the steam bath for four hours, replacing the evaporated acid

<sup>a</sup> Official and Provisional Methods of Analysis, U. S. Dept. of Agr., Bureau of Chemistry, Bul. 107.

from time to time. Dilute the solution, filter, and wash residue. Return filtrate to the porcelain dish, add 3 to 5 cc of concentrated arsenic-free sulphuric acid, and evaporate on the steam bath to a small bulk. Remove from the steam bath and treat on a hot plate till dense white fumes arise. Cool, dilute, boil, and filter into a 100 cc flask. Make up to the mark and use aliquot portions for determining arsenic by means of standard mirrors, or weighing the mirrors, in the Marsh-Berzelius apparatus, which method is described under the determination of arsenic in cattle-food materials. Test all reagents and apparatus by running a blank before using to be sure of absence of traces of arsenic.

*Total copper.*

Digest 10 grams of soil on the steam bath for four hours with 100 cc of 25 per cent nitric acid, using a porcelain evaporating dish with a watch-glass cover. Dilute, filter into a 500 cc flask, cool, and make up to the mark. Take an aliquot of 200 cc for analysis, nearly neutralize with ammonia, heat, and pass hydrogen sulphid through for about half an hour. Filter off the precipitate, wash, dry, and burn in a porcelain crucible. Add nitric acid to dissolve the precipitate and heat till the copper is dissolved. Filter through the smallest sized filter and determine copper by either of two methods according to the amount of this element present.

If copper is present in excess of 2 or 3 milligrams, proceed as follows: Neutralize the copper solution with sodium carbonate, adding a trifling excess of the latter. Add 1 cc of ammonia (sp. gr. 0.960) and titrate the dark-blue solution to the disappearance of the blue color with tenth-normal potassium cyanid which has been standardized against a known amount of copper by exactly the same method as that just described for the determination of the copper present.

If the copper is present in very minute quantities, proceed as follows: Add ammonium hydroxid to the copper solution until slightly in excess, heat on the steam bath a few minutes, filter on the smallest sized filter, wash, and evaporate the filtrate in a porcelain dish to 2 or 3 cc, cool, add acetic acid a drop at a time until the solution is just acid, and then add 5 drops of 4 per cent potassium ferrocyanid. Compare this color with the color produced by treating a known amount of copper dissolved in a similar amount of water in a porcelain dish with acetic acid and potassium ferrocyanid in exactly the same way as just described.

*Water-soluble copper.*

Weigh out 100 grams of soil, transfer to a flask, and treat with 1,000 cc of water. Shake the flask occasionally during eight hours, then let stand till the supernatant liquid is practically clear. Siphon off the clear liquid and filter. Evaporate a 750 cc aliquot of the liquid to dryness, take up the residue with 1 or 2 cc of nitric acid by the aid of heat, dilute, and filter. Heat the filtrate, pass hydrogen sulphid through for half an hour, filter, wash, dry, and burn the filter, and precipitate in a porcelain crucible. Add nitric acid to dissolve the precipitate and heat till the copper is dissolved. Filter through the smallest sized filter and determine copper by one of the methods described above under "Total copper."

*Soluble salts.*

Weigh out 50 grams of soil, transfer to a flask and treat with 1,000 cc of water, shake the flask occasionally during 8 hours and let stand till the supernatant liquid is practically clear. Siphon off the clear liquid and filter. Use

aliquots of the above liquid for determining carbonates, bicarbonates, chlorids, sulphates, calcium, magnesium, and sodium.

Follow the methods given for determining these constituents in waters in Bulletin 91, Bureau of Chemistry, U. S. Department of Agriculture, except in one particular, which is as follows:

When the salts are obtained in a hydrochloric acid solution, ready for the determination of calcium, magnesium, and sodium, pass through hydrogen sulphid to get rid of copper. Filter, evaporate to dryness, again take up in hydrochloric acid, and determine calcium, magnesium, and sodium in aliquots of this solution.

#### *Black alkali.<sup>a</sup>*

Solutions required: (1) A standard N/50 sodium carbonate solution. (2) A standard N/50 sulphuric acid solution. (3) A solution of erythrosin containing 0.25 gram to a liter of water. (4) Chloroform.

**METHOD:** Transfer 200 cc of the soil extract, obtained as in the preceding method, to a platinum dish, add 50 to 150 cc of standard sodium carbonate according to the amount of soluble salts of calcium and magnesium present, and evaporate to dryness. Rub the residue up with distilled carbon-dioxid-free water, transfer to a 100 cc graduated flask, make up to the mark, shake thoroughly, stopper, and allow to stand until clear. When clear, carefully remove 50 cc without disturbing the residue in the bottom of the flask and transfer to the titrating bottle. For this purpose use a bottle of the best colorless glass without any tinge of pink, with ground glass stopper and of about 250 cc capacity. Add 5 cc of chloroform and 1 cc of erythrosin and titrate the solution with the standard acid until the color disappears. The solution should be vigorously shaken after each addition of acid, the chloroform producing a milky appearance, which makes the reading of the end point sharp and certain.

If less sulphuric acid is required than that necessary to balance one-half of the sodium carbonate added, it is evident that some of the sodium carbonate has been used up and that the solution originally contained no black alkali. If, on the other hand, more sulphuric acid is required than that equivalent to one-half of the sodium carbonate added, then black alkali was originally present and can be calculated from the amount of standard sulphuric acid used in excess of that necessary to neutralize one-half the sodium carbonate originally added.

#### **WATERS.**

##### *Total copper.*

Shake sample thoroughly till well mixed with sediment and use 500 cc for analysis. Evaporate to dryness in a porcelain dish and determine total copper by the same methods used for total copper in soils.

##### *Soluble copper.*

Filter off 1,000 to 2,000 cc of the water from its sediment. Evaporate to dryness, take up with 1 or 2 cc of nitric acid by the aid of heat, dilute, filter, and determine soluble copper by the method used for soluble copper in soils.

##### *Soluble salts.*

Filter off 1,000 to 2,000 cc of the water from its sediment and determine carbonates, bicarbonates, chlorids, sulphates, calcium, magnesium, and sodium, according to the methods given for these constituents in waters in Bulletin 91, Bureau of Chemistry, U. S. Department of Agriculture.



## CATTLE-FOOD MATERIALS.

*Moisture.*

Use the method given for determining moisture in the foliage of trees (p. 34).

*Total arsenic.*

*Testing reagents.*—Make a blank on the reagents and apparatus by boiling down 100 cc of nitric acid and 5 cc of sulphuric acid in the same kind of flask used for treating the samples, diluting and boiling down again to get rid of final traces of nitric and nitrous acid, again diluting and finally running for two hours in the Marsh-Berzelius apparatus, described in the following section.

*Apparatus.*—This consists of a small flask with a wide mouth, holding about 100 cc. Through one hole of a rubber stopper a separatory funnel passes to the bottom of the flask. Through another hole in the rubber stopper passes the exit tube, which is in turn joined to a Liebig bulb containing a small amount of a solution of lead acetate to absorb any selenium, tellurium, or sulphur. This in turn is joined to a calcium chlorid tube, which is then attached to a long tube of very resistant glass. This glass tube is drawn out at one point rather small, nearly capillary, and the heat is applied about 0.5 inch before the drawn-out portion. Heat with two Bunsen burners, neither of which plays upon the glass directly but upon a piece of fine wire gauze wrapped around the glass. When preparing this apparatus for use, add about 3 grams of arsenic-free granulated zinc to the wide-mouthed bottle and then about 30 cc of arsenic-free sulphuric acid (1 to 8). Let the apparatus run for fifteen minutes, after which apply heat for approximately twenty minutes to be sure that no arsenic is present.

The apparatus is now ready for the addition of the extract from the cattle food. Run in and allow the action to continue for from one to two hours. Compare mirror thus formed with mirrors containing known amounts of arsenic, which have been previously prepared with the same apparatus. The standard mirrors usually contain the following amounts of arsenic: 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07 mg of arsenic. These mirrors should be in sealed tubes and be remade about every three weeks, as they tend to fade a little upon standing. When not in use, they should be kept in a dark place.

In case a larger amount than 0.07 mg of arsenic is obtained, cut off that part of the tube where the mirror is deposited, wipe carefully, and place in a desiccator. Then weigh on an assay balance capable of weighing to the fifth place. Dip the tube in sodium hypochlorite solution to dissolve the arsenic, wash with distilled water, then with alcohol, and finally with ether, dry, place in a desiccator, and weigh again. The difference in the two weights represents the arsenic from the amount of material taken. Both of these weighings must be made with the utmost care, as a small error at this point will cause a large error in the results.

*Standard solution.*—To prepare the standard solution, dissolve 0.5 gram of dry chemically pure arsenious oxid in a sodium carbonate solution (free from arsenic) by boiling. Make weakly acid with arsenic-free sulphuric acid and make up to a liter. Measure out such a quantity of this solution in a liter flask as will give 0.01 gram of metallic arsenic and make up to the mark. Each cubic centimeter of this solution represents 0.01 mg of arsenic and is used for making the standard mirrors.

*Method.*—Weigh 1 to 3 grams of the finely ground cattle food, according to the amount of arsenic present, and transfer to a 200 cc Jena flask. Add 25 cc

of concentrated arsenic-free nitric acid and 5 cc of concentrated arsenic-free sulphuric acid, allow the first violent action to subside, and then put on an iron plate and gradually heat to boiling. Continue boiling till the liquid begins to darken. When this occurs, add concentrated arsenic-free nitric acid in quantities of 3 cc at a time, until on further heating it continues colorless and fumes strongly of sulphuric acid. Cool, dilute with 10 cc of arsenic-free water, and boil to break up the nitro-sulphuric acid formed. When cool, dilute with water and deliver into the Marsh-Berzelius apparatus previously described.

*Soluble arsenic.*

Weigh from 1 to 3 grams of the finely ground cattle food, according to the amount of soluble arsenic present, and transfer to a beaker. Extract on the steam bath with 50 to 100 cc of water for four hours. Filter, wash, and evaporate the filtrate to a small bulk. Transfer to a 200 cc Jena flask and evaporate to only a few cubic centimeters. Add 25 cc of concentrated arsenic-free nitric acid and 5 cc of concentrated arsenic-free sulphuric acid and proceed as in the preceding method for total arsenic.

**ORES.**

*Sulphur.<sup>a</sup>*

Treat 0.5 gram of the ore in a 6-oz. flask with 10 cc of strong nitric acid. Heat very gently until the red fumes have somewhat abated, and then add potassium chlorate in small portions at a time (about 0.2 to 0.3 gram) until any free sulphur that has separated is entirely oxidized and dissolved. The acid should not be boiled violently, nor should it simply simmer. When the sulphur has entirely disappeared, boil the solution to complete dryness. (This may be hastened by manipulating the flask over a free flame.) After cooling cautiously add 5 cc of strong hydrochloric acid. If iron oxid, etc., still remains undissolved, gently heat the hydrochloric acid mixture until solution is as complete as possible, adding more acid, if necessary. Finally boil to dryness. Repeat this operation. Take up once more in 5 cc of hydrochloric acid and dilute with about 100 cc of hot water. Make alkaline with ammonia and then add 10 cc of a saturated solution of ammonium carbonate in order to convert any lead sulphate present to carbonate and thus render the combined SO<sub>2</sub> soluble as ammonium sulphate. Heat to boiling, allow ferric hydroxid, etc., to settle, filter, and wash very thoroughly with hot water, receiving the filtrate in a large beaker.

Neutralize with hydrochloric acid and add 5 cc extra. Dilute to about 300 cc and precipitate with barium chlorid in the ordinary way.

*Arsenic.<sup>a</sup>*

Thoroughly mix 0.5 gram of the finely ground ore in a large platinum crucible with 5 grams of a mixture of equal parts of dry sodium carbonate and potassium nitrate. Reserve a portion of the mixed salts for use as a cover. Heat the mass gradually over a Bunsen flame to complete fusion. Use a very low flame at first and take plenty of time to avoid loss of arsenic by volatilization. Finally heat to the full power of the Bunsen burner until thoroughly decomposed. The melted mass should finally present a smooth and homogeneous appearance. Cool, extract the soluble portion by heating with water, and filter and wash the residue with hot water. Drop a piece of litmus paper into the filtrate and make slightly acid with nitric acid, adding enough to dis-

solve any precipitate that may have formed. Add a sufficient quantity of a solution of silver nitrate, which will usually cause a white precipitate of silver chlorid, and then cautiously add ammonia until, if arsenic be present, a reddish precipitate of silver arsenate appears. If too much ammonia be added the precipitate first formed will redissolve and may not be observed at all. Cautiously add dilute nitric acid until the red precipitate just redissolves. To the faintly acid liquid add a few cubic centimeters of a strong solution of sodium acetate to replace the free nitric acid by acetic acid. All the arsenic will now at once precipitate as silver arsenate ( $\text{Ag}_3\text{AsO}_4$ ).

Heat the precipitated mixture to boiling, cool to room temperature, and filter. If the first portions run through turbid, return them to the filter. Test the filtrate with a little more silver nitrate and sodium acetate. Wash the precipitate with cold water until a portion of the washings shows only a faint test for silver.

Place the original flask under the funnel and dissolve the arsenate on the filter with cold 1:1 nitric acid. Wash the filter thoroughly with cold water, leaving behind on the filter any silver chlorid that may be present. Dilute the filtrate, add 5 cc of a strong solution of ammonium ferric alum and titrate to a permanent red tinge with a standard solution of ammonium thiocyanate, shaking well, especially toward the end. Multiply the number of cubic centimeters required by the arsenic equivalent of each cubic centimeter.

Standardize the sulphocyanate solution against a known weight of pure silver dissolved in nitric acid. From the equivalent of each cubic centimeter of the sulphocyanate in silver the equivalent of each cubic centimeter in arsenic can be calculated from the formula  $\text{Ag}_3\text{AsO}_4$ .

## O











